



⑩ Offenlegungsschrift
⑪ DE 3104215 A1

⑩ Int. Cl. 3:
C 12P 17/18
C 12 N 1/14
A 61 K 31/48

DE 3104215 A1

⑩ Aktenzeichen:
⑩ Anmeldetag:
⑩ Offenlegungstag:

P 31 04 215.6
8. 2. 81
18. 8. 82

⑩ Anmelder:
Richter Gedeon Vegyészeti Gyár R.T., 1103 Budapest, HU
⑩ Vertreter:
Bezárdes, S., Dipl.-Chem. Dr.rer.nat., Pat.-Anw., 8060
Dachau

⑩ Erfinder:
Nagy, geb. Cserey Pechamy, Eva Udvary, Dr.; Budai,
Miklós, Dipl.-Chem. Ing.; Fekete, György, Dr.; Görög,
Sándor, Dipl.-Chem. Ing. Dr.; Herényi, Bulcsú,
Dipl.-Pharm.; Wack, Gázs; Zsai, Károly, Dipl.-Pharm.,
Budapest, HU

⑩ Verfahren zur Herstellung von Alkaloiden in geregelter Menge und geregeltem Mengenverhältnis durch Gärung

Gegenstand der Erfindung ist ein Verfahren zur Herstellung von Alkaloiden in geregelter Menge und geregeltem Mengenverhältnis durch Gärung von unter saprophytischen Bedingungen, vor allem Ergoconin, α - und β -Ergocryptin erzeugenden Variantenstämme von Claviceps purpurea, bei welchem bei der Gärung als Regler eine oder mehr in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindung(en) und/oder eine oder mehr durch biochemische Regelung die Bildung des Isoleucines anregende Verbindung(en) verwendet wird bzw. werden.
(31 04 215)

DE 3104215 A1

- 2 -

Patentansprüche

- 1.) Verfahren zur Herstellung von Alkaloiden in geregelter Menge und geregeltem Mengenverhältnis durch Gärung von unter saprophytischen Bedingungen, vor allem Ergoçornin, α - und β -Ergocryptin erzeugenden, Variantenstämmen von *Claviceps purpurea*, dadurch gekennzeichnet, daß man bei der Gärung als Regler 1 oder mehr in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindung(en) und/oder 1 oder mehr durch biochemische Regelung die Bildung des Isoleucines anregende Verbindung(en) verwendet.
- 2.) Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man als in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindung(en) Methyloxalessigsäure, α -Ketobuttersäure, Threonin und/oder Homoserin verwendet.
- 3.) Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß man als durch biochemische Regelung die Bildung des Isoleucines anregende Verbindung(en) Homocystein und/oder Methionin verwendet.
- 4.) Verfahren nach Anspruch 1 bis 3, dadurch gekennzeichnet, daß man den Regler in einer Menge von 0,01 bis 10 kg/m³ Fermentbrühe, insbesondere 0,05 bis 5,0 kg/m³ Fermentbrühe, verwendet.

Beschreibung

06.02.61

3104215

DR. STEPHAN G. BESZEDES

PATENTANWALT

VNR: 101 265

ZUGELASSENER VERTRETER
AUCH BEIM EUROPÄISCHEN PATENTAMT

PROFESSIONAL REPRESENTATIVE ALSO
BEFORE THE EUROPEAN PATENT OFFICE

8060 DACHAU BEI MÜNCHEN
POSTFACH 1168

MÜNCHENER STRASSE 80A

Bundesrepublik Deutschland

TELEPHON: DACHAU 4271

Postcheckkonto München (BLZ 700 100 80)

Bankkonto-Nr. 696-275 bei der Kreis- und Stadt-

Kapitalei Dachau-Isenadorf (BLZ 700 515 40)

(VIA Bayrische Landesbank

(Girozentrale, München)

P 1 416

Patentansprüche und Beschreibung

zur Patentanmeldung

RICHTER GEDEON VEGYESZETI GYÁR R.T.

Budapest, Ungarn

betreffend

Verfahren zur Herstellung von Alkaloiden
in geregelter Menge und geregeltem Men-
genverhältnis durch Gärung

- 3 -

B e s c h r e i b u n g

Die Erfindung betrifft ein Verfahren zur Herstellung von Alkaloiden in geregelter Menge und geregeltem Mengenverhältnis durch Gärung beziehungsweise Fermentation von unter saprophytischen Bedingungen, vor allem Ergocornin, α - und β -Ergocryptin erzeugenden, Variantenstämmen von *Claviceps purpurea*.

Es ist bekannt, daß das Dihydroergotoxinmethansulfonat beziehungsweise Dihydroergotoxinäthansulfonat in der Medizin als Regler des zentralen Stoffwechsels sowie des zentralen und peripheren Kreislaufs verwendet wird. Diese Verbindungen erhöhen die Proteinsynthese des Zentralnervensystems und hemmen die von den Brenzatechinaminen angeregte beziehungsweise stimulierte Adenylzyklase. Ferner wirken sie schwach sedativ, hemmen die Reflexatrichardie, verbessern die Gehirndurchblutung und senken den Blutdruck. In der Medizin werden sie vor allem zur Behandlung von Krankheiten, welche auf peripheren Kreislaufstörungen oder Gehirnkreislaufstörungen beruhen, angewandt.

Das Dihydroergotoxin wird durch Hydrieren des Ergotoxins hergestellt. Das erhaltene Produkt ist ein Gemisch aus Dihydroergocristin, Dihydroergocornin und Dihydroergocryptin (ungarische Patentschrift 129 061). Das Dihydroergocryptin liegt in 2 verschiedenen Modifikationen (α - und β -Form) vor (Experientia 23 [1967], 991).

- 4 -

und nach neuesten Untersuchungen ist die pharmakologische Wirkung der beiden Formen nicht ganz identisch. Die α -Form erwies sich bei einem Empfängnisverhütungsversuch an Ratten als aktiver, während die β -Form an enthirnten (decerebrierten) Katzen eine stärkere Vasopressorwirkung hatte (Experientia 33 [1977], 1 552). Aus diesem Grund ist in den Vorschriften für dihydroergotixinhaltige Präparate das Mengenverhältnis von α - und β -Dihydroergocryptin festgelegt. Für ideal wird das Verhältnis der α -Form zur β -Form von 2 : 1 gehalten und das Dihydroergotoxin optimaler Zusammensetzung enthält die Bestandteile Dihydroergocristin, Dihydroergocornin, α -Dihydroergocryptin und β -Dihydroergocryptin im Mengenverhältnis von 3 : 3 : 2 : 1. Die zulässigen Toleranzen bezüglich des Mengenverhältnisses von α -Dihydroergocryptin zu β -Dihydroergocryptin sind in den einzelnen Ländern verschieden. In den USA und mehreren europäischen Ländern liegen die zulässigen Grenzwerte des Gehaltes an β -Dihydroergocryptin bei 26,7 bis 44 Gew.-% des Gesamtgehaltes an Dihydroergocryptin, während in anderen europäischen Ländern und in Japan die Toleranz bei 28,6 bis 40 Gew.-% liegt.

Die Anfangsstufe der Herstellung von Dihydroergotoxin-methansulfonat beziehungsweise Dihydroergotininäthansulfonat ist die Herstellung der nicht hydrierten Mutterkornalkaloide (Ergocristin, Ergocornin, α - und β -Ergocryptin).

Diese Alkaloide werden auf biologischem Wege hergestellt. Eine Möglichkeit dazu ist die parasitäre Biosynthese, nach welcher Roggen infiziert und das erzeugte Alkaloid durch Drogenextraktion gewonnen wird. Dieses Verfahren wird hauptsächlich bei der Herstellung von

Ergocristin angewandt [verwendete Stämme: der in der American Type Culture Collection unter der Nummer ATCC 20103 hinterlegte, in der britischen Patentschrift 1 192 912 beschriebene Stamm und der von Richter Gedeon Vegyészeti Gyár RT, Budapest, Ungarn unter der Nummer MNG 00163 in der Nationalen Stammsammlung des ungarischen Landesinstitutes für Gesundheitswesen (Országos Közegészségügyi Intézet) hinterlegte Stamm].

Ferner kann die Biosynthese auch auf saprophytischem Wege erfolgen, wobei die Alkaloide aus der Gärbrühe isoliert werden. Die bekanntesten Stämme für dieses Verfahren sind der Ergocryptin und Ergotamin erzeugende bei der American Type Culture Collection unter der Nummer ATCC 20102 hinterlegte Stamm (britische Patentschrift 1 158 380), der Ergocornin und Ergosin erzeugende bei der American Type Culture Collection unter der Nummer ATCC 20106 hinterlegte Stamm (britische Patentschrift 1 184 039), der Ergocryptin erzeugende bei der American Type Culture Collection unter der Nummer ATCC 20019 hinterlegte Stamm (US-Patentschrift 3 485 772), der B-Ergocryptin und Ergosin erzeugende Stamm der Soc. Farmaceutici Italia (in deren eigener Sammlung unter Nr. FI 7374 hinterlegt und in der belgischen Patentschrift 824 987 beschrieben).

Daraus ist ersichtlich, daß diese selektierten Stämme nicht nur die für die Herstellung des Ergotoxins wichtigen Alkaloide erzeugen, sondern auch andere Mutterkornalkalide, das heißt, daß ihre Gärung nicht selektiv auf Ergotoxin orientiert ist.

Von ungarischen Forschern wurden zum ersten Mal Stämme

06.02.81

3104215

- 6 -

von *Claviceps purpurea*, die hauptsächlich α - und β -Ergocryptin erzeugen, selektiert [ungarische Patentschrift 152 238, Hinterlegungsnr. MNG 0022 bei der Nationalen Stammsammlung des ungarischen Landesinstitutes für Gesundheitswesen (Orezágos Közegészságügyi Intézet); ungarische Patentschrift 164 816, Hinterlegungsnr. MNG 0088 bei der Nationalen Stammsammlung des ungarischen Landesinstitutes für Gesundheitswesen (Országos Közegészságügyi Intézet)]. Auch mit diesen Stämmen ist jedoch die Einstellung des Mengenverhältnisses der Alkaloide zueinander während der Gärung nicht geregelt. Das Verhältnis der 3 erzeugten Alkaloide zueinander kann nur nachträglich eingestellt werden, indem das erhaltene Alkaloidgemisch durch die zur Verfügung stehenden umständlichen Verfahren in seine Bestandteile zerlegt wird und diese im entsprechenden Verhältnis erneut miteinander vermischt werden.

Ferner ist ein Verfahren, bei welchem 2 Stämme, von denen der eine Ergocornin, Ergocryptin und deren Isomere und der andere Ergocristin erzeugt, gleichzeitig gegoren werden, bekannt (schweizerische Patentschrift 577 556). Aus der gemeinsamen Kulturflüssigkeit der beiden Stämme werden die aufgeführten Alkaloide in einem nicht näher bezeichneten Verhältnis gewonnen. Eine Regelung dieses Verhältnisses wird auch bei diesem Verfahren nicht erreicht. Problematisch ist ferner, daß die Gärung beim gleichzeitigen Einsatz von 2 Stämmen viel schwerer beherrschbar werden kann als in einem Verfahren, bei welchem nur das Züchtungsoptimum eines einzigen Stammes berücksichtigt werden muß.

Von H. Kobel wurde (in seinem 1977 in Basel auf der Sitzung der Federation of the European Microbiological

- 7 -

(Societies gehaltenen Vortrag) festgestellt, daß die Biosynthese der Peptidalkalioide durch bestimmte Aminosäuren beeinflußt werden kann. Die Biosynthese des α -Peptidteile Valin enthaltenden Ergocornins kann durch Zusatz von Valin und die Biosynthese des Leucin enthaltenden α -Ergocryptines durch Zusatz von Leucin gefördert werden. Hingegen kann die Biosynthese des Isoleucin enthaltenden β -Ergocryptines durch Zusatz von Isoleucin nicht beeinflußt werden. Als wahrscheinlicher Grund für diese merkwürdige Erscheinung wurde von Kobel angegeben, daß das Wachstum der zur Erzeugung von β -Ergocryptin befähigten Stämme durch Isoleucin gehemmt wird.

Da in den Kulturbriühen der bekannten Ergocryptin oder Ergocornin und Ergocryptin erzeugenden Stämme eben der Anteil des β -Ergocryptines kleiner als erforderlich ist, konnte das geeignete Verhältnis weiterhin nicht eingestellt werden.

Auch hinsichtlich der erzeugten Menge der gewünschten Alkalioide insgesamt lassen die bekannten Verfahren zu wünschen übrig.

Der Erfindung liegt die Aufgabe zugrunde, unter Behebung der Nachteile des Standes der Technik ein Verfahren zur Herstellung von Alkaloiden durch Gärung von unter saprophytischen Bedingungen, vor allem Ergocornin, α - und β -Ergocryptin erzeugenden, Variantenstämmen von *Claviceps purpurea*, bei welchem diese Gärung in günstiger Richtung, das heißt im Sinne der höheren Erzeugung des β -Ergocryptines und/oder der Erzeugung der einzelnen Alkalioide im für die Ergotoxinerzeugung gewünschten Mengenverhältnis

und/oder der höheren Erzeugung der für das Ergotoxin gebrauchten Alkaloide insgesamt beeinflußt wird, zu schaffen.

Das Obige wurde überraschenderweise durch die Erfindung erreicht.

Es wurde nämlich überraschenderweise festgestellt, daß der zu geringe Anteil an β -Ergocryptin in der Gärbrühe ansteigt, wenn die Alkaloiderzeugung der Variantenstämme von *Claviceps purpurea* statt mit Isoleucin mit 1 oder mehr in der Biosynthese des Isoleucines als Vorstufe wirkenden Verbindung(en) beeinflußt wird. Die Vorstufen des Isoleucines hemmen demnach das Wachstum der genannten Stämme nicht.

Ferner wurde überraschenderweise festgestellt, daß die Alkaloiderzeugung auch mit Verbindungen, die durch biochemische Regelung die Bildung des Isoleucines anregen beziehungsweise stimulieren, geregelt werden kann.

Weiterhin wurde überraschenderweise festgestellt, daß durch die in der Biosynthese des Isoleucines als Vorstufe wirkende(n) Verbindung(en) beziehungsweise durch biochemische Regelung die Bildung des Isoleucines anregende(n) Verbindung(en) auch eine höhere Erzeugung der für das Ergotoxin gebrauchten Alkaloide insgesamt erreicht werden kann.

Gegenstand der Erfindung ist daher ein Verfahren zur Herstellung von Alkaloiden in geregelter Menge und geregeltem Mengenverhältnis durch Gärung von unter saprophytischen Bedingungen, vor allem Ergocornin, α - und β -Ergocryptin erzeugenden, Variantenstämmen von *Claviceps purpurea*, welches dadurch gekennzeichnet ist, daß bei der

Gärung als Regler 1 oder mehr in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindung(en) sind/oder 1 oder mehr durch biochemische Regelung die Bildung des Isoleucines anregende beziehungsweise stimulierende Verbindung(en) verwendet wird beziehungsweise werden.

In der Biosynthese des Isoleucines als Vorstufe wirkende Verbindungen sind in Lehninger, Biochemistry, Worth Publ. Inc. N. Y. [1975], Seite 704 beschrieben.

Als in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindungen und durch biochemische Regelung die Bildung des Isoleucines anregende Verbindungen werden vor allem Ketosäuren, Hydroxysäuren und Aminosäuren mit 4 bis 6 Kohlenstoffatomen, deren Biosynthese von der Asparaginsäure oder deren Phosphat ausgeht, verwendet.

Die in der Biosynthese des Isoleucines als Vorstufe wirkenden Verbindungen sind in der Reihenfolge ihrer Bildung die folgenden: Über Homoserin und Threonin oder 3-Methylasparaginsäure (2-Amino-3-methylbernsteinsäure und Methyloxallessigsäure (2-Methyl-3-oxobernsteinsäure) α -Ketobuttersäure, daran anschließend α -Acetyl- α -hydroxybuttersäure, α , β -Dihydroxy- β -methylvaleriansäure und α -Keto- β -methylvaleriansäure. In erfundungsgemäßen Verfahren wird beziehungsweise werden bevorzugt Methyloxallessigsäure, α -Ketobuttersäure, Threonin und/oder Homoserin verwendet.

Die durch biochemische Regelung die Bildung des Isoleucines anregenden beziehungsweise stimulierenden Verbindungen gehören biochemisch den sogenannten Aspartaten, das heißt Verbindungen, deren Biosynthese von der

- 10 -

Asparaginsäure oder deren Phosphat ausgeht, an. In erster Linie handelt es sich um Ketosäuren, Hydroxysäuren und Aminosäuren mit 4 bis 6 Kohlenstoffatomen. Bevorzugt wird beziehungsweise werden erfindungsgemäß Homocystein und/oder Methionin verwendet.

Vorzugsweise wird beziehungsweise werden der beziehungsweise die Regler in einer Menge von 0,01 bis 10 kg/m^3 Fermentbrühe, insbesondere 0,05 bis $5,0 \text{ kg/m}^3$ Fermentbrühe, verwendet. Es ist auch bevorzugt, den Regler in Form einer wässrigen, gegebenenfalls schwach sauren Lösung nach dem Sterilisieren des Nährmediums zuzusetzen, und zwar auf einmal, in mehreren Portionen oder in einer der Perioden der Gärung kontinuierlich.

Im erfindungsgemäßen Verfahren werden bevorzugt die folgenden Variantenstämme von *Claviceps purpurea* verwendet:

Claviceps purpurea, hinterlegt am 24. April 1963
unter der Bezeichnung MNG 0022,

Claviceps purpurea, hinterlegt am 25. Januar 1972
unter der Bezeichnung MNG 0088 und

Claviceps purpurea, hinterlegt am 9. Mai 1979
unter der Bezeichnung MNG 00186,

jeweils bei der Nationalen Stammsammlung des ungarischen Landesinstitutes für Gesundheitswesen (Országos Közegészségügyi Intézet).

Im Falle der Verwendung des Variantstammes Claviceps purpurea MNG 00186 wird das B-Ergocryptin bereits ohne Regler in hohen Mengenanteil erhalten. Erfindungsgemäß wurde nun überraschenderweise festgestellt, daß in diesem Falle bei Verwendung der erfindungsgemäß festgelegten Regler das Mengenverhältnis der erzeugten Alkaloide sich kaum ändert, die Gesamtmenge der Alkaloide und damit auch der für das Ergotoxin gebrauchten Alkaloide in der Gärbrühe sich jedoch erhöht.

Zweckmäßig wird die Gärung in submerser Kultur unter aerenen Bedingungen an einem Kohlenstoff- und Stickstoffquellen und Mineralsalze sowie gegebenenfalls sonstige Zusätze enthaltenden flüssigen Nährmedium, vorzugsweise bei 20 bis 26°C und einem pH-Wert von 5,2 bis 6,8 4 bis 8 Tage lang, durchgeführt.

Im Schrifttum wird der Gehalt der Gärbrühe an Alkaloiden häufig durch spektrophotometrisch gemessene Werte angegeben. Der Gesamtalkaloidgehalt wurde auch im vorliegenden Falle spektrophotometrisch gemessen, die Meßergebnisse waren jedoch nicht spezifisch.

Die einzelnen Ergotoxinbestandteile wurden durch Elutionschromatographie beziehungsweise quantitative Flüssigkeitschromatographie getrennt bestimmt.

Die Erfindung wird an Hand der folgenden Beispiele näher erläutert.

06.02.81

3104215

- 12 -

Beispiel 1

Es wurden 200 cm³ eines weiter unten beschriebenen Nährmediums GK in einem 500 cm³ Erlenmeyerkolben mit einer auf einem weiter unten beschriebenen Agarnährmedium AIC gezüchteten Kultur des Stammes *Claviceps purpurea* MNG 0022 geimpft. Der Erlenmeyerkolben wurde bei 24°C auf einem Schütteltisch mit einer Frequenz von 300 Minute⁻¹. 3 Tage lang bebrütet. Das dabei erhaltene Impfmaterial beziehungsweise Inoculum wurde auf 5 l eines weiter unten beschriebenen Nährmediums St in einer 10 l Gärvorrichtung überimpft. Die Kultur wurde bei 24°C und einer Rührgeschwindigkeit von 240 Umdrehungen/Minute unter Belüftung mit 0,5 l Luft je 1 Gärbrühe und Minute 7 Tage lang gezüchtet. In der 40-sten, 64-sten, 88-sten und 112-sten Stunde wurde der Gärbrühe als in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindung eine 10%-ige wässrige Lösung von Methyloxalessigäure in einer 0,5 g Methyloxalessigäure (Trockensubstanz)/l Gärbrühe entsprechenden Menge zugesetzt. Das Mengenverhältnis der Alkalioide Ergocornin und Ergocryptin erreichte am 7-ten Tag der Gärung den gewünschten Wert. Der mittels Farbreaktion messbare Gesamtgehalt an Alkaloiden betrug 1 150 µ/cm³. Die dünnenschichtchromatographische Bestimmung (J. of Chrom. 87 [1973], 433) ergab 300 µ/cm³ Ergocornin, 180 µ/cm³ Ergocryptin und 110 µ/cm³ von deren rechtsdrehendem Epi-mer. Das Verhältnis von α -Ergocryptin zu β -Ergocryptin betrug gemäß der Untersuchung mittels Hochdruckflüssigkeitschromatographie (J. Pharm. Sci. 67 [1978], 98) 66 : 34.

Die Alkalioide wurden aus der Gärbrühe in an sich bekannter Weise isoliert.

Die verwendeten Nährmedien hatten die folgenden Zusammensetzungen:

- 13 -

06.02.81

3104215

- 13 -

Nährmedium GK

Trypcasin	7,0 g
Citronensäure	4,1 g
Kaliumdihydrogenphosphat	0,3 g
Magnesiumsulfat	0,3 g
Ammoniak bis zur Erreichung eines pH-Wertes von 5,7 bis 5,8	
Wasser	bis 840 cm ³

Je 84 cm³ oder 168 cm³ des Nährmediums wurden in Kolben gefüllt. In jeden Kolben wurden 16 cm³ beziehungsweise 32 cm³ einer 50%-igen Glucoselösung eingebracht.

Agarnährmedium AIC

Mannit	40,0 g
Citronensäure	7,0 g
Maisquellwasser	2,0 g
Kaliumdihydrogenphosphat	1,0 g
Magnesiumsulfat	0,3 g
Agarpulver (Difco)	25,0 g
Ammoniak bis zur Erreichung eines pH-Wertes von 5,2 bis 5,3	
Wasser	bis 1 000 cm ³

Der gewünschte pH-Wert des Nährmediums wurde während des Aufkochens eingestellt. Dann wurde das Nährmedium in Portionen von je 6 cm³ in Reagenzgläser gefüllt und durch Schrägstellen der Gläser als Schrägagar erstarrten gelassen.

- 14 -

Nährmedium St

Saccharose	100,0 g
Bernsteinsäure	10,0 g
Kaliumdihydrogenphosphat	0,25 g
Magnesiumsulfat	0,25 g
Ammoniumnitrat	1,0 g
Calciumchlorid	1,0 g
Ammoniak	bis zur Erreichung eines pH-Wertes von 5,2 bis 5,3
Wasser	bis 1 000 cm ³

Das Nährmedium wurde in Portionen von je 0,1 l
oder 5 l oder 100 l sterilisiert.

Beispiel 2

Es wurden 200 cm³ eines im Beispiel 1 beschriebenen Nährmediums GK in einem 750 cm³ Erlenmeyerkolben mit der auf einem im Beispiel 1 beschriebenen Agarnährmedium AIG gezüchteten Kultur des Variantstamms *Claviceps purpurea* MNG 0088 geimpft. Die Kultur wurde bei 24°C auf einem Schütteltisch mit einer Frequenz von 300 Minute⁻¹ 3 Tage lang bebrütet. Die erhaltene Kultur wurde auf 5 l eines weiter unten beschriebenen Nährmediums TG 54 in einer 10 l Laboratoriumsgärvorrichtung überimpft. Die Kultur wurde bei 24°C und einer Rührgeschwindigkeit von 240 Umdrehungen/Minute unter Belüftung mit 0,5 l Luft je 1 Gärbrühe und Minute 3 Tage lang bebrütet. Mit dem

- 15 -

- 15 -

erhaltenen Impfmaterial beziehungsweise Inoculum wurden 100 l eines im Beispiel 1 beschriebenen Nährmediums St in einer mit einem Rührer versehenen säurefesten Gärvorrichtung geimpft und die Kultur wurde bei 24°C und einer Rührgeschwindigkeit von 120 Umdrehungen/Minute unter Belüftung mit 0,3 l Luft je 1 Gärbrühe und Minute 6 Tage lang gegoren. In den ersten 5 Tagen der Gärung wurde der Kultur als in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindung eine 5%-ige wäßrige α -Ketobuttersäurelösung mit einer Zuführungsgeschwindigkeit von 20 cm³/Stunde zugesetzt.

Nach dem Abbrechen der Gärung betrug der Gesamtalkalidgehalt 920 γ/cm^3 . Mit der im Beispiel 1 angegebenen hochdruckflüssigkeitschromatographischen Verfahrensweise wurden 260 γ/cm^3 Ergocornin, 155 γ/cm^3 α -Ergocryptin und 95 γ/cm^3 β -Ergocryptin nachgewiesen; außerdem war noch ein Gehalt an 80 γ/cm^3 Ergocorcorninin und Ergocryptinin (Ergocorninin ergocryptinin) meßbar.

Das Nährmedium TC 54 hatte die folgende Zusammensetzung:

Saccharose	100,0 g
Citronensäure	10,0 g
Natriumchlorid	10,0 g
Kaliumdihydrogenphosphat	0,5 g
Magnesiumsulfat	0,5 g
Ammoniak	bis zur Erreichung eines pH-Wertes von 5,7 bis 5,8
Wasser	bis 1 000 cm ³

Das Nährmedium wurde in Portionen von je 5 l in einer Laboratoriumsgärvorrichtung sterilisiert.

- 16 -

Beispiel 3

Es wurden 100 cm³ eines im Beispiel 1 beschriebenen Nährmediums GK in einem 500 cm³ Erlenmeyerkolben mit der auf einem weiter unten beschriebenen Agarnährmedium St gezüchteten Kultur des Variantstamms *Claviceps purpurea* MNG 0088 geimpft. Die Kultur wurde bei 24°C auf einem Schütteltisch mit einer Frequenz von 300 Minute⁻¹ 3 Tage lang bebrütet. 10 cm³ der erhaltenen Kultur wurden auf 100 cm³ eines weiter unten beschriebenen Nährmediums T 25 überimpft. Diese Kultur wurde bei 20°C ebenfalls auf dem Schütteltisch 5 Tage lang bebrütet. In der 20-sten Stunde wurde die Gärbrühe mit 0,5 g Threonin als in der Biosynthese des Isoleucins als Vorstufe wirkende Verbindung versetzt. Am 5-ten Tag betrug die Gesamtaalkaloidkonzentration 1 200 γ/cm³. Mit der im Beispiel 1 angegebenen hochdruckflüssigkeitschromatographischen Verfahrensweise wurden 260 γ/cm³ Ergocornin, 140 γ/cm³ α-Ergocryptin und 80 γ/cm³ β-Ergocryptin nachgewiesen; der Gesamtgehalt an Ergocorninin und Ergocryptinin betrug 130 γ/cm³.

Die verwendeten Nährmedien hatten die folgenden Zusammensetzungen:

Agrarnährmedium St

Das Agarnährmedium St unterschied sich vom im Beispiel 1 beschriebenen flüssigen Nährmedium St darin, daß ihm je Liter 25 g Agarpulver (Difco) zugesetzt wurden. Nach dem Zusatz des Agars wurde das Nährmedium aufgekocht, dann in Portionen von je 5 cm³ in Reagenzgläser gefüllt, sterilisiert und durch Schrägstellen der Gläser zu Schräggagar erstarrten gelassen.

06.02.61

3104215

- 17 -

Nährmedium T 25

Saccharose	300,0 g
Citronensäure	15,0 g
Hefeextrakt	1,0 g
Kaliumdihydrogenphosphat	0,5 g
Magnesiumsulfat	0,5 g
Ammoniak bis zur Erreichung eines pH-Wertes von 5,2 bis 5,3	
Wasser	bis 1 000 cm ³

Das Nährmedium wurde in Portionen von je 100 cm³
in Kolben gefüllt und sterilisiert.

Beispiel 4

Es wurde wie im Beispiel 3 beschrieben gearbeitet, jedoch als in der Biosynthese des Isoleucines als Vorstufe wirkende Verbindung 0,5 g Homoserin statt des Threonines verwendet. Am 5-ten Tag der Gärung betrug der Gesamtgehalt an Alkaloiden 880 µ/cm³. Die Gärbrühe enthielt 220 µ/cm³ Ergocornin, 150 µ/cm³ α -Ergocryptin und 80 µ/cm³ β -Ergocryptin; Ergocorninin und Ergocryptinin machten zusammen 180 µ/cm³ aus.

- 18 -

- 18 -

Beispiel 5

Es wurde wie im Beispiel 3 beschrieben gearbeitet, jedoch 0,05 g Homocystein als durch biochemische Regelung die Bildung des Isoleucines anregende Verbindung statt des Threonines verwendet. Am 5-ten Tag betrug die Gesamtalkaloidkonzentration $700 \text{ } \mu\text{/cm}^3$. Die Gärbrühe enthielt $190 \text{ } \mu\text{/cm}^3$ Ergocornin, $85 \text{ } \mu\text{/cm}^3$ α -Ergocryptin und $90 \text{ } \mu\text{/cm}^3$ β -Ergocryptin; Ergocorninin und Ergocryptinin machten zusammen $150 \text{ } \mu\text{/cm}^3$ aus.

Beispiel 6

Es wurden 100 cm^3 eines im Beispiel 1 beschriebenen Nährmediums GK in einem 500 cm^3 Erlenmeyerkolben mit der auf einem im Beispiel 3 beschriebenen Agarnährmedium St gezüchteten Kultur des Stammes *Claviceps purpurea* MNG 00186 geimpft. Die Kultur wurde bei 24°C auf einem Schütteltisch mit einer Frequenz von 300 Minute^{-1} 4 Tage lang bebrütet. Je 10 cm^3 der erhaltenen Kultur wurden in 8 Kolben, die je 100 cm^3 eines im Beispiel 1 beschriebenen Nährmediums St enthielten, eingebracht. Die Kulturen wurden bei 24°C ebenfalls auf dem Schütteltisch 7 Tage lang gegoren. In 4 Kolben wurde keine durch biochemische Regelung die Bildung des Isoleucines anregende Verbindung eingebracht. In die anderen 4 Kolben wurden in der 24-sten und 48-ten Stunde der Gärung je 0,02 g Methionin in Lösung in je 2 cm^3 Wasser eingebracht. Am 7-ten Tag wurde die Gärung abgebrochen.

- 19 -

- 19 -

Die ohne Zusatz der durch biochemische Regelung die Bildung des Isoleucines anregenden Verbindung erhaltenen Gärbrühen wurden vereinigt und die Bestimmung ihres Alkaloidgehaltes ergab: 80 γ/cm^3 Ergocornin, 15 γ/cm^3 α -Ergocryptin und 30 γ/cm^3 β -Ergocryptin.

Die mit der durch biochemische Regelung die Bildung des Isoleucines anregenden Verbindung erhaltenen Gärbrühen wurden ebenfalls vereinigt und untersucht. Es wurden 250 γ/cm^3 Ergocornin (durchschnittlicher Gehalt), 50 γ/cm^3 α -Ergocryptin und 100 γ/cm^3 β -Ergocryptin nachgewiesen.

Zusammenfassung

⑤

Int. Cl. 2:

⑯ BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES



PATENTAMT

A 01 N 21/02

DT 26 25 398 A 1

⑩

Offenlegungsschrift 26 25 398

⑪

Aktenzeichen: P 26 25 398.5

⑫

Anmeldetag: 5. 6. 76

⑬

Offenlegungstag: 15. 12. 77

⑭

Unionspriorität:

⑮ ⑯ ⑰

—

⑯

Bezeichnung:

Mittel und Verfahren zum Stimulieren des Keimens von Kartoffeln

⑮

Anmelder:

Philips Patentverwaltung GmbH, 2000 Hamburg

⑯

Erfinder:

Moldovany, Nikolaus, Dipl.-Ing.agr., 4010 Hilden;
Kohl, Wilhelm, Dipl.-Chem. Dr., 4047 Dormagen;
Schneider, Alfred, Dipl.-Ing.agr. Dr., 4005 Meerbusch

DT 26 25 398 A 1

Patentansprüche:

1) Mittel zum Stimulieren des Keimens von Kartoffeln, gekennzeichnet durch folgende Zusammensetzung:

16	bis	30	Gew.% Calciumglycerophosphat
und/oder			
$1,6 \cdot 10^{-5}$	bis	$3 \cdot 10^{-5}$	Gew.% Calciumpantothenat
sowie			
0,002	bis	0,012	Gew.% Cystein
und			
$3,2 \cdot 10^{-5}$	bis	$4 \cdot 10^{-5}$	Gew.% Kinetin,

Rest: Füll- und Trägerstoffe, wie Aluminiumsilikat, z.B. Kaolin, Aluminiumoxid oder Siliciumdioxid.

2. Mittel nach Anspruch 1, dadurch gekennzeichnet, daß es zusätzlich einen oder mehrere der folgenden Stoffe enthält:

10	bis	24	Gew.% Ammoniumsulfat
20	bis	40	Gew.% Kaliumnitrat
8	bis	16	Gew.% Glucose
8	bis	16	Gew.% Saccharose
0,8	bis	1,6	Gew.% Bernsteinsäure
0,1	bis	0,3	Gew.% Citronensäure
0,1	bis	0,3	Gew.% Weinsäure
0,1	bis	0,3	Gew.% Äpfelsäure
0,4	bis	0,5	Gew.% Natriumbenzoat
0,002	bis	0,004	Gew.% Tyrosin
0,008	bis	0,02	Gew.% Inositol
0,002	bis	0,006	Gew.% Ascorbinsäure
$1,6 \cdot 10^{-5}$	bis	$3 \cdot 10^{-5}$	Gew.% Thiamin
$5 \cdot 10^{-5}$	bis	$9 \cdot 10^{-5}$	Gew.% Biotin
$3,2 \cdot 10^{-5}$	bis	$4 \cdot 10^{-5}$	Gew.% Indolyl-3-essigsäure.

- / -

3. Mittel nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß es zusätzlich ein oder mehrere Fungizide enthält.

4. Verfahren zum Stimulieren des Keimens von Kartoffeln mit dem Mittel nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß die Kartoffeln vor dem Setzen 2 bis 10 min in eine 0,03- bis 0,3 gew.%ige wäßrige Lösung des Mittels getaucht werden.

PHILIPS PATENTVERWALTUNG GMBH, Steindamm 94, 2000 Hamburg 1

Mittel und Verfahren zum Stimulieren des Keimens von Kartoffeln

Die Erfindung betrifft ein Mittel zum Stimulieren des Keimens von Kartoffeln und ein Verfahren, bei dem das Mittel angewendet wird.

Um bei Kartoffeln eine vorzeitige Reife zu erzielen, werden die Kartoffeln in einer künstlichen Atmosphäre zum Vorkiemen gebracht. Dies erfordert besondere Gebäude, in denen die Kartoffeln in niedriger Schütt Höhe mehrere Tage dem Einfluß von Wärme und Licht ausgesetzt werden. Da die so hervorgerufenen

709850/0420

PHD 76-104

Jü

- 2 -

Keime leicht abbrechen, sind besonders schonend arbeitende Kartoffellegemaschinen erforderlich, die einen hohen Arbeits- und Zeitaufwand mit sich bringen.

Der Erfindung liegt die Aufgabe zugrunde, diesen Aufwand zu vermeiden.

Diese Aufgabe wird erfindungsgemäß durch ein Mittel der ein- gangs genannten Art gelöst, das durch folgende Zusammensetzung gekennzeichnet ist:

16 bis 30 Gew.% Calciumglycerophosphat
und/oder
 $1,6 \cdot 10^{-5}$ bis $3 \cdot 10^{-5}$ Gew.% Calciumpantothenat
sowie
0,002 bis 0,012 Gew.% Cystein
und
 $3,2 \cdot 10^{-5}$ bis $4 \cdot 10^{-5}$ Gew.% Kinetin,

Rest: Füll- und Trägerstoffe, wie Aluminiumsilikat, z.B. Kaolin, Aluminiumoxid oder Siliciumdioxid.

In einer bevorzugten Ausführungsform enthält das erfindungs- gemäßige Mittel zusätzlich noch einen oder mehrere der folgenden Stoffe:

10	bis	24	Gew.% Ammoniumsulfat
20	bis	40	Gew.% Kaliumnitrat
8	bis	16	Gew.% Glucose
8	bis	16	Gew.% Saccharose
0,8	bis	1,6	Gew.% Bernsteinsäure
0,1	bis	0,3	Gew.% Citronensäure
0,1	bis	0,3	Gew.% Weinsäure
0,1	bis	0,3	Gew.% Äpfelsäure
0,4	bis	0,5	Gew.% Natriumbenzoat

- / -

0,002	bis	0,004	Gew.% Tyrosin
0,008	bis	0,02	Gew.% Inosit
0,002	bis	0,006	Gew.% Ascorbinsäure
$1,6 \cdot 10^{-5}$	bis	$3 \cdot 10^{-5}$	Gew.% Thiamin
$5 \cdot 10^{-5}$	bis	$9 \cdot 10^{-5}$	Gew.% Biotin
$3,2 \cdot 10^{-5}$	bis	$4 \cdot 10^{-5}$	Gew.% Indolyl-3-essigsäure.

Da Saatkartoffeln häufig vor dem Setzen mit Fungiziden, z.B. gegen Phytophthora infestans, behandelt werden, ist es zweckmäßig, dem erfindungsgemäßen Mittel ein oder mehrere Fungizide zuzusetzen. Dies erspart gegenüber dem bisher üblichen Vorkeimen einen Arbeitsgang.

Die Keimstimulierung mit Hilfe des erfindungsgemäßen Mittels wird vorzugsweise so vorgenommen, daß Saatkartoffeln vor dem Setzen 2 bis 10 min, insbesondere 5 min, in eine 0,03- bis 0,3 gew.%ige wässrige Lösung des Mittels getaucht werden. Dabei haftet das erfindungsgemäße Mittel hauptsächlich an den Augen der Kartoffeln fest. Man kann das erfindungsgemäße Mittel aber auch als Stäubepulver formulieren, indem man z.B. anorganische Trägerstoffe zusetzt.

Die Erfindung beruht demnach auf dem Gedanken, das Vorkeimen von Kartoffeln durch eine Behandlung mit einem chemischen Mittel zu ersetzen.

Die Vorteile der Erfindung bestehen gegenüber nicht vorgekeimten Kartoffeln in einem Zeitvorsprung, der fast genauso groß ist wie bei vorgekeimten Kartoffeln, gegenüber vorgekeimten Kartoffeln in einer sehr großen Arbeitsersparnis.

Die Erfindung wird nachfolgend anhand eines Ausführungsbeispiels näher erläutert. Es wurde folgendes Gemisch hergestellt:

Calciumglycerophosphat	10,000 kg
Ammoniumsulfat	10,000 kg
Kaliumnitrat	16,000 kg
Glucose	6,010 kg
Saccharose	6,010 kg
Bernsteinsäure	0,601 kg
Citronensäure	0,121 kg
Weinsäure	0,121 kg
Äpfelsäure	0,121 kg
Natriumbenzoat	0,241 kg
Tyrosin	0,002 kg
Inosit	0,006 kg
Ascorbinsäure	0,001 kg
Thiamin	12 mg
Calciumpantothenat	12 mg
Biotin	36 mg
Cystein	0,003 kg
Kinetin	18 mg
Indolyl-3-essigsäure	18 mg
Aluminiumsilicat (Attagel® 40)	<u>0,763 kg</u>
	<u>50,000 kg</u>
	=====

Aus diesem pulverförmigen Gemisch wurde kurz vor dem Behandeln von Saatkartoffeln eine 0,3 gew.%ige wässrige Lösung bereitet.

709850/0420

- 5 -

In diese Lösung wurden die Saatkartoffeln 5 min lang getaucht und sodann gesetzt.

Bei einem Vergleichsanbau wurde festgestellt, daß der Zeitvorsprung der mit dem erfundungsgemäßen Mittel vorbehandelten Kartoffeln 80 bis 90 % der auf übliche Weise vorgekeimten Kartoffeln betrug. Andererseits beträgt die Zeit- und Arbeitersparnis infolge des Fortfalls der Vorkeimung 200 bis 250 %.

Patentansprüche:

- 6 -

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
1 July 2004 (01.07.2004)

PCT

(10) International Publication Number
WO 2004/054525 A1

(51) International Patent Classification⁷: A61K 7/06, 7/50

(21) International Application Number:
PCT/EP2003/013700

(22) International Filing Date:
25 November 2003 (25.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02258603.6 13 December 2002 (13.12.2002) EP

(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, SI, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CORNWELL, Paul, Alfred [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63

3JW (GB), HULL, Peter, James [GB/GB]; 19 Valley Way, Knutsford, Cheshire WA16 9AH (GB), SKINNER, Richard [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(74) Agents: TANSLEY, Sally, Elizabeth et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE (utility model), DZ, EC, EE (utility model), ES, FI (utility model), GL, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NL, NO, NZ, OM, PG, PH, PL, PT (utility model), PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (BW, GH, GI, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/054525 A1

(54) Title: HAIR TREATMENT COMPOSITIONS

(57) Abstract: The invention provides a hair treatment composition such as a shampoo or conditioner comprising a disaccharide and a diol.

- 1 -

HAIR TREATMENT COMPOSITIONS

FIELD OF THE INVENTION

5

The invention relates to hair treatment compositions. More particularly the invention relates to hair treatment compositions comprising specific combinations of active materials. The compositions are particularly suitable for 10 application to hair for repair and restoration of damaged hair.

BACKGROUND AND PRIOR ART

15 Hair can suffer damage from a number of sources such as; exposure to UV and chlorine; chemical influences such as bleaching, perming, overly frequent washing with harsh surfactant-based cleansing shampoo compositions; and mechanical influences such as prolonged use of heated 20 styling appliances.

Damage to the hair typically manifests itself in cuticle and protein loss from the hair fibre, hair fibre brittleness and breakage and frayed or split ends.

25

In addition consumers require their hair to be manageable; that is that the hair when styled will retain that style for a long period of time and in a range of environmental detrimental conditions such as high humidity.

30

The use of sugars and plant extracts are disclosed in WO 01/68040 (L'oreal) to protect keratinous tissue.

5 The present invention has now found that compositions comprising certain specific combinations of sugars and alcohols are effective for repairing and preventing the principal symptoms of damaged hair, these combinations also have the further advantage that they help to increase the
10 manageability of the hair.

DESCRIPTION OF THE INVENTION

In a first aspect, the present invention provides a hair
15 treatment composition comprising a disaccharide and a diol, wherein the diol is not propylene glycol or butylene glycol.

A further aspect of the invention is the use of the above composition for smoothing hair, aligning hair and preventing
20 damage to the hair.

The invention also relates to a method of treating hair by applying the above composition to the hair.

25 Detailed Description

The disaccharide

The present invention comprises as an essential element of
30 the invention a disaccharide, preferably the disaccharide

- 3 -

comprises of pentose or hexose sugars, more preferably the disaccharide comprises of two hexose units.

Disaccharides can be either reducing or non-reducing sugars.

5 Non-reducing sugars are preferred.

The D(+) form of the sugars are preferred. Particularly preferred are trehalose and cellobiose or mixtures thereof. Trehalose is the most preferred disaccharide.

10

It is preferable if the disaccharide is not in the form of a salt and/or not sulphated.

15 The level of disaccharides present in the total formulation is preferably from 0.1wt% to 10wt%, more preferably from 0.2wt% to 5wt%, most preferably from 0.5wt% to 2wt%.

Diols

20 It is preferable if the diol has from 2 to 10 carbon atoms, preferably 3 to 6 carbon atoms, most preferably the diol has 4 carbon atoms.

25 I is advantageous if the diol has its hydroxyl groups positioned on C1 and C3 positions within the carbon backbone.

An especially preferred form of the diol is 3-methyl, 1,3, butanediol.

30

- 4 -

In addition diols are best used at a diol:disaccharide weight ratios of from 0.1:1 to 1:0.1, preferably from 0.1:1 and 2:1, most preferably from 2:1 to 1:2.

5 The level of diol present in the total formulation is preferably from 0.1wt% to 10wt%, more preferably from 0.2wt% to 5wt%, most preferably from 0.5wt% to 2wt%.

10 The pH of the formulations of the invention are in the range from pH 3 to pH 6, more preferably used at pH 3-5.

Product Form

15 The final product form of hair treatment compositions according to the invention may suitably be, for example, shampoos, conditioners, sprays, mousses, gels, waxes or lotions. Particularly preferred product forms are shampoos, post-wash conditioners (leave-in and rinse-off) and hair treatment products such as hair essences. Rinse-off 20 compositions are particularly preferred.

Shampoo compositions preferably comprise one or more cleansing surfactants, which are cosmetically acceptable and suitable for topical application to the hair. Further 25 surfactants may be present as emulsifiers.

Suitable cleansing surfactants, are selected from anionic, amphoteric and zwitterionic surfactants, and mixtures

- 5 -

thereof. The cleansing surfactant may be the same surfactant as the emulsifier, or may be different.

Anionic Cleansing Surfactant

5

Shampoo compositions according to the invention will typically comprise one or more anionic cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair.

10

Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, 15 alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, 20 alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule.

- 6 -

Typical anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl sulpho succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium cocoyl isethionate, sodium lauryl 5 isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3), ammonium lauryl sulphate and ammonium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3).

10

The total amount of anionic cleansing surfactant in shampoo compositions of the invention is generally from 5 to 30, preferably from 6 to 20, more preferably from 8 to 16 wt%.

15 **Co-surfactant**

The shampoo composition can optionally include co-surfactants, preferably an amphoteric or zwitterionic surfactant, which can be included in an amount ranging from 0 20 to about 8, preferably from 1 to 4 wt%.

Examples of amphoteric and zwitterionic surfactants include, alkyl betaines, alkyl amidopropyl betaines, alkyl

- 7 -

sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinate, alkyl amphopropionate, alkylamphoglycinate, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

10

Another preferred co-surfactant is a nonionic surfactant, which can be included in an amount ranging from 0 to 8, preferably from 2 to 5 wt%.

15 For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic (C₈ - C₁₈) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having 20 from 6 to 30 ethylene oxide groups.

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides

(APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:

5



wherein R is a branched or straight chain C₅ to C₂₀ alkyl or alkenyl group, G is a saccharide group and n is from 1 to 10.

10

Other sugar-derived nonionic surfactants which can be included in shampoo compositions of the invention include the C₁₀-C₁₈ N-alkyl (C₁-C₆) polyhydroxy fatty acid amides, such as the C₁₂-C₁₈ N-methyl glucamides, as described for example in WO 15 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide.

The shampoo composition can also optionally include one or more cationic co-surfactants included in an amount ranging 20 from 0.01 to 10, more preferably from 0.05 to 5, most preferably from 0.05 to 2 wt%. Useful cationic surfactants are described hereinbelow in relation to conditioner compositions.

- 9 -

The total amount of surfactant (including any co-surfactant, and/or any emulsifier) in shampoo compositions of the invention is generally from 5 to 50, preferably from 5 to 30, more preferably from 10 to 25 wt%.

5

Cationic Polymer

A cationic polymer may be present. The cationic polymer may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally 10 be between 5 000 and 10 000 000, typically at least 10 000 and preferably in the range 100 000 to about 2 000 000. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof.

Suitable cationic nitrogen polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition

The cationic conditioning polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

- 10 -

Suitable cationic conditioning polymers include, copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (CTFA name Polyquaternium-16); copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate, (CTFA name Polyquaternium-11); cationic diallyl quaternary ammonium-containing polymers in particular (CTFA Polyquaternium 6 and Polyquaternium 7, mineral acid salts of amino-alkyl esters of homo-and copolymers of unsaturated carboxylic acids as described in U.S. Patent 4,009,256; cationic polyacrylamides (as described in WO95/22311).

Cationic polysaccharide polymers suitable for use in compositions of the invention include those with an anhydroglucose residual group, such as a starch or cellulose. Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl

- 11 -

ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimonium chloride (commercially available from Rhone-Poulenc in their JAGUAR trademark series). Particularly preferred cationic polymers are JAGUAR C13S, JAGUAR C14, JAGUAR C15, JAGUAR C17 and JAGUAR C16 Jaguar CHT and JAGUAR C162.

The cationic conditioning polymer will generally be present in compositions of the invention at levels of from 0.01 to 5, preferably from 0.05 to 1, more preferably from 0.08 to 0.5

Conditioning Surfactant

Conditioner compositions usually comprise one or more conditioning surfactants, which are cosmetically acceptable

5 and suitable for topical application to the hair.

Suitable conditioning surfactants are selected from cationic surfactants, used singly or in admixture.

10 Cationic surfactants useful in compositions of the invention contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention.

15 Examples of suitable cationic surfactants are those corresponding to the general formula:



20 in which R_1 , R_2 , R_3 , and R_4 are independently selected from (a) an aliphatic group of from 1 to 22 carbon atoms, or (b) an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to 22 carbon atoms; and X

- 13 -

is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

5

The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or
10 unsaturated.

The most preferred cationic surfactants for conditioner compositions of the present invention are monoalkyl quaternary ammonium compounds in which the alkyl chain
15 length is C16 to C22.

Examples of suitable cationic surfactants include quaternary ammonium compounds, particularly trimethyl quaternary compounds.

20

Preferred quaternary ammonium compounds include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride (BTAC), cetylpyridinium chloride,

- 14 -

tetramethylammonium chloride, tetraethylammonium chloride,
octyltrimethylammonium chloride, dodecyltrimethylammonium
chloride, hexadecyltrimethylammonium chloride,
octyldimethylbenzylammonium chloride,
5 decyldimethylbenzylammonium chloride,
stearyldimethylbenzylammonium chloride,
didodecyldimethylammonium chloride,
dioctadecyldimethylammonium chloride, tallowtrimethylammonium
chloride, cocotrimethylammonium chloride, PEG-2 oleylammonium
10 chloride and salts of these where the chloride is replaced
by halogen, (e.g. , bromide), acetate, citrate, lactate,
glycolate, phosphate nitrate, sulphate, or alkylsulphate.
Further suitable cationic surfactants include those materials
having the CTFA designations Quaternium-5, Quaternium-31 and
15 Quaternium-18. Mixtures of any of the foregoing materials
may also be suitable. A particularly useful cationic
surfactant for use in hair conditioners of the invention is
cetyltrimethylammonium chloride, available commercially, for
example as GENAMIN CTAC, ex Hoechst Celanese.

20

Salts of primary, secondary, and tertiary fatty amines are
also suitable cationic surfactants. The alkyl groups of such

amines preferably have from 12 to 22 carbon atoms, and can be substituted or unsubstituted.

Particularly useful are amido substituted tertiary fatty amines, in particular tertiary amines having one C₁₂ to C₂₂ alkyl or alkenyl chain. Such amines, useful herein, include

5 stearamidopropylidimethylamine,
stearamidopropyldiethylamine, stearamidoethyldiethylamine,
stearamidoethylidimethylamine, palmitamidopropylidimethylamine, palmitamidopropyldiethylamine,
10 behenamidopropylidimethylamine,
behenamidopropyldiethylamine, behenamidoethyldiethylamine,
behenamidoethylidimethylamine,
15 arachidamidopropylidimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine,
arachidamidoethylidimethylamine, diethylaminoethylstearamide.
Also useful are
dimethylstearamine, dimethylsoyamine, soyamine,
20 myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and arachidyl behenylamine.

- 16 -

These amines are typically used in combination with an acid to provide the cationic species. The preferred acid useful herein includes L- glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, 5 tartaric acid, citric acid, L-glutamic hydrochloride, and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055 to Nachtigal, et al., issued June 23, 1981.

10

The molar ratio of protonatable amines to H^+ from the acid is preferably from about 1:0.3 to 1:1.2, and more preferably from about 1:0.5 to about 1:1.1.

15 In the conditioners of the invention, the level of cationic surfactant is preferably from 0.01 to 10, more preferably 0.05 to 5, most preferably 0.1 to 2 wt% of the total composition.

20 The cationic surfactants detailed in this section are also suitable for use in the aspect of the invention wherein a cationic surfactant is intimately mixed with the thermotropic mesogenic material and with oily conditioning

- 17 -

material prior to the incorporation of the conditioning material into the final hair conditioning composition

Fatty Materials

5

Conditioner compositions of the invention preferably additionally comprise fatty materials. The combined use of fatty materials and cationic surfactants in conditioning compositions is believed to be especially advantageous, 10 because this leads to the formation of a structured phase, in which the cationic surfactant is dispersed.

By "fatty material" is meant a fatty alcohol, an alkoxyolated fatty alcohol, a fatty acid or a mixture thereof.

15

Preferably, the alkyl chain of the fatty material is fully saturated.

Representative fatty materials comprise from 8 to 22 carbon 20 atoms, more preferably 16 to 22. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and mixtures thereof. The use of these materials is also advantageous in

- 18 -

that they contribute to the overall conditioning properties of compositions of the invention.

AlkoxyLATED, (e.g. ethoxylated or propoxylated) fatty
5 alcohols having from about 12 to about 18 carbon atoms in
the alkyl chain can be used in place of, or in addition to,
the fatty alcohols themselves. Suitable examples include
ethylene glycol cetyl ether, polyoxyethylene (2) stearyl
ether, polyoxyethylene (4) cetyl ether, and mixtures
10 thereof.

The level of fatty alcohol material in conditioners of the
invention is suitably from 0.01 to 15, preferably from 0.1 to
10, and more preferably from 0.1 to 5 wt%. The weight ratio
15 of cationic surfactant to fatty alcohol is suitably from 10:1
to 1:10, preferably from 4:1 to 1:8, optimally from 1:1 to
1:7, for example 1:3.

20 **Suspending Agents**

In a preferred embodiment, the hair treatment composition,
especially if it is a shampoo composition, further comprises
from 0.1 to 5-wt% of a suspending agent. Suitable suspending

- 19 -

agents are selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of 5 acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof. Ethylene glycol 10 distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used; they are available commercially as 15 Carbopol 910, Carbopol 934, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trademark) materials are available from Goodrich.

20

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

25

- 20 -

Conditioning Agents

Silicone Conditioning Agents

The compositions of the invention can contain emulsified
5 droplets of a silicone conditioning agent, for enhancing
conditioning performance.

Suitable silicones include polydiorganosiloxanes, in
particular polydimethylsiloxanes that have the CTFA
10 designation dimethicone. Also suitable for use compositions
of the invention (particularly shampoos and conditioners)
are polydimethyl siloxanes having hydroxyl end groups, which
have the CTFA designation dimethiconol. Also suitable for
use in compositions of the invention are silicone gums
15 having a slight degree of cross-linking, as are described
for example in WO 96/31188.

The viscosity of the emulsified silicone itself (not the
emulsion or the final hair conditioning composition) is
20 typically at least 10,000 cst at 25 °C the viscosity of the
silicone itself is preferably at least 60,000 cst, most
preferably at least 500,000 cst, ideally at least 1,000,000

- 21 -

cst. Preferably the viscosity does not exceed 10³ cst for ease of formulation.

Emulsified silicones for use in the shampoo compositions of 5 the invention will typically have an average silicone droplet size in the composition of less than 30, preferably less than 20, more preferably less than 10 μm , ideally from 0.01 to 1 μm . Silicone emulsions having an average silicone droplet size of $\leq 0.15 \mu\text{m}$ are generally termed 10 microemulsions.

Examples of suitable pre-formed emulsions include emulsions DC2-1766, DC2-1784, DC-1785 DC-1786 and microemulsions DC2-1865 and DC2-1870, all available from Dow Corning. These 15 are all emulsions/microemulsions of dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation. A preferred example is the material available from Dow Corning as DC X2-1787, which is an emulsion of cross-linked 20 dimethiconol gum. A further preferred example is the material available from Dow Corning as DC X2-1391, which is a microemulsion of cross-linked dimethiconol gum.

- 22 -

A further preferred class of silicones for inclusion in shampoos and conditioners of the invention are amino functional silicones. By "amino functional silicone" is meant a silicone containing at least one primary, secondary 5 or tertiary amine group, or a quaternary ammonium group.

Examples of suitable amino functional silicones include: polysiloxanes having the CTFA designation "amodimethicone", Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, 10 DC2-8166, DC2-8466, and DC2-8950-114 (all ex Dow Corning), and GE 1149-75, (ex General Electric Silicones).

Suitable quaternary silicone polymers are described in EP-A-0 530 974. A preferred quaternary silicone polymer is K3474, ex Goldschmidt.

15 Also suitable are emulsions of amino functional silicone oils with non-ionic and/or cationic surfactant. Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow 20 Corning and General Electric. Specific examples include DC929 Cationic Emulsion, DC939 Cationic Emulsion, and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all ex Dow Corning).

- 23 -

With some shampoos it is particularly preferred to use a combination of amino and non amino functional silicones

The total amount of silicone is preferably from 0.01 to 10
5 %wt of the total composition more preferably from 0.3 to 5;
most preferably 0.5 to 3-wt% is a suitable level.

(ii) Non-silicone Oily Conditioning Components

10 Compositions according to the present invention may also comprise a dispersed, non-volatile, water-insoluble oily conditioning agent.

By "insoluble" is meant that the material is not soluble in
15 water (distilled or equivalent) at a concentration of
0.1% (w/w), at 25°C.

Suitable oily or fatty materials are selected from hydrocarbon oils, fatty esters and mixtures thereof.

20 Straight chain hydrocarbon oils will preferably contain from about 12 to about 30 carbon atoms. Also suitable are polymeric hydrocarbons of alkenyl monomers, such as C₂-C₆ alkenyl monomers.

Specific examples of suitable hydrocarbon oils include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and 5 unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used.

10

Suitable fatty esters are characterised by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, Monocarboxylic acid esters include esters of alcohols and/or acids of the 15 formula R'COOR in which R' and R independently denote alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20. Di- and trialkyl and alkenyl esters of carboxylic acids can also be used.

20 Particularly preferred fatty esters are mono-, di- and triglycerides, more specifically the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as C₁-C₂₂ carboxylic acids. Preferred materials include cocoa

- 25 -

butter, palm stearin, sunflower oil, soyabean oil and coconut oil.

The oily or fatty material is suitably present at a level of 5 from 0.05 to 10, preferably from 0.2 to 5, more preferably from about 0.5 to 3-wt%.

In hair treatment compositions containing a conditioning agent, it is preferred that a cationic polymer also be 10 present.

Styling polymers

If the product is a styling product it is preferred if a styling polymer is present

15 The hair styling polymer if present is preferably present in the compositions of the invention in an amount of from 0.001% to 10% by weight, more preferably from 0.1% to 10% by weight, such as from 1% to 8% by weight.

20 Hair styling polymers are well known. Suitable hair styling polymers include commercially available polymers that contain moieties that render the polymers cationic, anionic, amphoteric or nonionic in nature. Suitable hair styling 25 polymers include, for example, block and graft copolymers. The polymers may be synthetic or naturally derived.

Adjuvants

The compositions of the present invention may also contain adjuvants suitable for hair care. Generally such 5 ingredients are included individually at a level of up to 2, preferably up to 1 wt% of the total composition.

Suitable hair care adjuvants, include amino acids and ceramides.

10

The invention will now be further illustrated by the following, non-limiting Examples.

15 A number illustrates examples of the invention; a letter illustrates Comparative Examples.

All percentages quoted are by weight based on total weight unless otherwise stated.

EXAMPLES

The following Examples were prepared:

5 Table 1Shampoo

Ingredients	Wt %	
	Example A	Example 1
Sodium laurylether sulphate(2EO)	12	12
Cocoyl amidopropyltrimethyl glycine	2	2
Silicone emulsion	2	2
Guar hydroxypropyl trimethylammonium chloride	0.30	0.30
Preservative	0.35	0.35
Perfume	0.42	0.42
Citric acid	0.17	0.17
Trimethyl glycine	1.20	-
Trehalose	-	0.70
3-methyl 1,3-butanediol		0.70
Water and minors	to 100 wt%	

10 Results were obtained from a panel of sixty consumers. Each product was tested sequentially for a period of four days, with three days in-between, using a product without any

- 28 -

actives. The results show consumer assessed scores of the Examples relative to the Comparative Example.

The results are shown in figure 1 . It is clearly shown
5 that Example 1 has significant advantages over the
comparative Example (Example A)

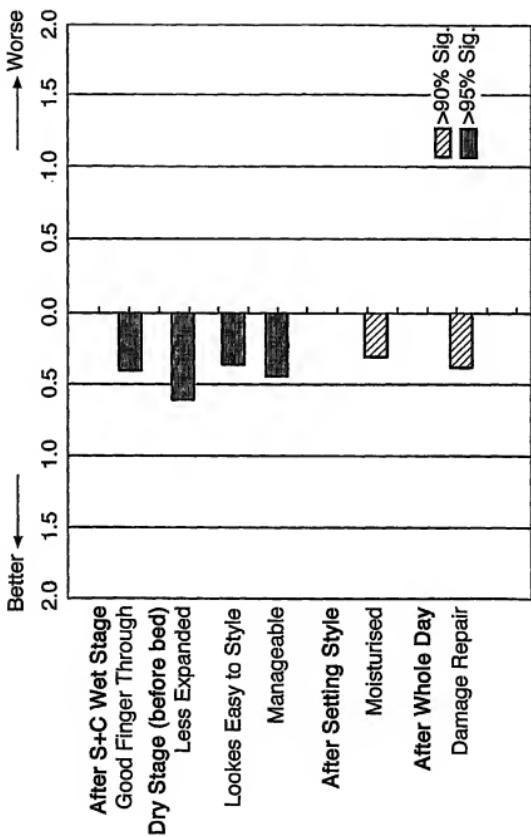
CLAIMS

1. A hair treatment composition comprising a disaccharide and a diol, wherein the diol is not propylene glycol or butylene glycol.
5
2. A hair treatment composition according to claim 1 in which the disaccharide has two hexose rings.
- 10 3. A hair treatment composition according to any preceding claim in which the disaccharide is selected from trehalose, cellobiose or mixtures thereof.
- 15 4. A hair treatment composition according to any preceding claim in which the disaccharide is trehalose.
5. A hair treatment composition according to any preceding claim in which the diol has from 2 to 10 carbon atoms.
- 20 5. A hair treatment composition according to any preceding claim in which the diol has its hydroxyl groups positioned on C1 and C3.
- 25 6. A hair treatment composition according to any preceding claim in which the diol has 4 carbon atoms.
7. A hair treatment composition according to claim 6 in which the diol is 3-methyl, 1,3, butanediol.
- 30 8. A hair treatment composition according to any proceeding claim further comprising a surfactant.

- 30 -

9. A hair treatment composition according to any preceding claim comprising an aqueous base.
- 5 10. Use of a composition according to any preceding claim for smoothing hair.
11. Use of a composition according to any one of claims 1 to 9 for aligning hair.
- 10 12. Use of a composition according to any one of claims 1 to 9 for preventing damage to the hair.
13. A method of treating hair by applying a composition according to any one of claims 1 to 9 to the hair.
- 15

Fig. 1.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/13700A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/06 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 06, 4 June 2002 (2002-06-04) & JP 2002 047168 A (POLA CHEM IND INC), 12 February 2002 (2002-02-12) abstract	1-13
X	US 4 690 818 A (PUCHALSKI JR EUGENE ET AL) 1 September 1987 (1987-09-01) column 5, line 31 - line 35; claim 1; example 1	1,5,8-13
A	EP 0 691 407 A (HAYASHIBARA BIOCHEM LAB) 10 January 1996 (1996-01-10) page 35; examples B-17	1-13

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel; it may be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

A document member of the same patent family

Date of the actual completion of the International search	Date of mailing of the International search report
20 April 2004	29/04/2004
Name and mailing address of the ISA European Patent Office, P.B. 5816 Patentsteen 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax. (+31-70) 340-3016	Authorized officer Voyiazoglou, D

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/13700

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 839 164 A (SMITH WALTER P) 13 June 1989 (1989-06-13) claims 1,4; example 1 -----	1-13
A	WO 00/47167 A (COLOR ACCESS INC) 17 August 2000 (2000-08-17) page 8, line 22; examples II,III -----	1-13
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 10, 31 October 1996 (1996-10-31) & JP 08 157339 A (LION CORP), 18 June 1996 (1996-06-18) abstract -----	1,5-13
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 10, 30 November 1995 (1995-11-30) & JP 07 173488 A (AJINOMOTO CO INC), 11 July 1995 (1995-07-11) abstract -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/13700

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
JP 2002047168	A	12-02-2002	NONE			
US 4690818	A	01-09-1987	NONE			
EP 0691407	A	10-01-1996	JP CA DE DE EP ES TW US	8073504 A 2152563 A1 69528019 D1 69528019 T2 0691407 A1 2182869 T3 426736 B 5919666 A	19-03-1996 28-12-1995 10-10-2002 22-05-2003 10-01-1996 16-03-2003 21-03-2001 06-07-1999	
US 4839164	A	13-06-1989	CA	1322532 C		28-09-1993
WO 0047167	A	17-08-2000	AU WO	2416400 A 0047167 A1	29-08-2000 17-08-2000	
JP 08157339 8	A		NONE			
JP 07173488 8	A		NONE			

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
1 July 2004 (01.07.2004)

PCT

(10) International Publication Number
WO 2004/054526 A1

(51) International Patent Classification⁷: A61K 7/06, 7/50

(21) International Application Number:
PCT/EP2003/013701

(22) International Filing Date:
26 November 2003 (26.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02258604.4 13 December 2002 (13.12.2002) EP

(71) Applicant (for AE, AG, AU, BB, BZ, CA, CG, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NI, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, SY, TD, TG, TI, TM, TN, TR, UA, UZ, VN, YU only): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CORNWELL, Paul, Alfred [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). HULL, Peter, James [GB/GB]; 19 Valley

Way, Knutsford, Cheshire WA16 9AH (GB). SKINNER, Richard [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). DEVINE, Karen, Marla [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(74) Agents: TANSLEY, Sally, Elizabeth et al.; Unilever PLC, Patent Department, Colworth House, Shambrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, EG, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JE, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NL, NO, NZ, OM, PG, PH, PL, PT (utility model), PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TI, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HAIR TREATMENT COMPOSITIONS

(57) Abstract: The invention provides a hair treatment composition such as a shampoo or conditioner comprising a disaccharide and a di-acid.

WO 2004/054526 A1

- 1 -

HAIR TREATMENT COMPOSITIONS

FIELD OF THE INVENTION

5

The invention relates to hair treatment compositions. More particularly the invention relates to hair treatment compositions comprising specific combinations of active materials. The compositions are particularly suitable for 10 application to hair for repair and restoration of damaged hair.

BACKGROUND AND PRIOR ART

15 Hair can suffer damage from a number of sources such as; exposure to UV and chlorine; chemical influences such as bleaching, perming, overly frequent washing with harsh surfactant-based cleansing shampoo compositions; and mechanical influences such as prolonged use of heated 20 styling appliances.

Damage to the hair typically manifests itself in cuticle and protein loss from the hair fibre, hair fibre brittleness and breakage and frayed or split ends.

25

In addition consumers require their hair to be manageable; that is that the hair when styled will retain that style for a long period of time and in a range of environmental detrimental conditions such as high humidity.

30

- 2 -

WO 97/14401 (Kao Corporation) describes a wide range of organic acids in skin and hair care compositions.

The use of sugars and plant extracts are disclosed in
5 WO 01/68040 (L'Oréal) to protect keratinous tissue.

Trehalose has been used to improve the elasticity of skin and/or prevent ageing as disclosed in WO 01/01948.

The present invention has now found that compositions
10 comprising certain specific combinations of sugars and acids are effective for repairing and preventing the principal symptoms of damaged hair, these combinations also have the further advantage that they help to increase the manageability of the hair.

15

DESCRIPTION OF THE INVENTION

In a first aspect, the present invention provides a hair treatment composition comprising i) from 0.05 wt.% to
20 49 wt.% of a disaccharide; and ii) a di- acid.

A further aspect of the invention is the use of the above composition for smoothing hair, aligning hair and preventing damage to the hair.

25

The invention also relates to a method of treating hair by applying the above composition to the hair.

Detailed Description**The disaccharide**

5

The present invention comprises as an essential element of the invention a disaccharide, preferably the disaccharide comprises of pentose or hexose sugars, more preferably the disaccharide comprises of two hexose units.

10

Disaccharides can be either reducing or non-reducing sugars. Non-reducing sugars are preferred.

15 The D(+) form of the sugars are preferred. Particularly preferred are trehalose and cellobiose or mixtures thereof. Trehalose is the most preferred disaccharide.

20 The level of disaccharides present in the total formulation is from 0.05 wt% to 49 wt%, more preferably from 0.2wt% to 3 wt%, most preferably from 0.5wt% to 2wt%.

Di-Acids

25 Di-acids are present in the compositions of the present invention, particularly suitable are di-acids having the formula:



30 where n is an integer from 2 to 8, more preferably where n equal to 2 or 4 (succinic acid and adipic acid respectively).

- 4 -

Organic acids are best used at levels in the total formulation from 0.01 wt% to 5wt%, more preferably at levels from 0.1wt% to 2wt%.

5

The weight ratio of di-acid to disaccharide is 1:10 to 20:1, more preferably 1:5 to 5:1.

In addition, acids are best used at di-acid:disaccharide 10 molar ratios of between 0.1:1 and 10:1, preferably between 0.1:1 and 2:1.

The pH of the formulations of the invention are in the range from pH 3 to pH 6, more preferably used at pH 3-5.

15

Guanidinium Salt

Optionally a guanidinium salt is present. For example, 20 guanidinium carbonate, guanidinium sulphate and guanidinium phosphate. Particularly preferred is guanidinium carbonate. Guanidinium salts are best used at levels from 0.01wt% to 5wt.% of the total formulation, more preferably at 0.1wt% to 2wt%.

25

The preferred weight ratio of guanidinium salt to disaccharide is from 1:10 to 4:1, more preferably 2:1 to 1:2.

- 5 -

In addition the preferred guanidinium salt:disaccharide molar ratios are from 0.1:1 to 10:1, more preferably from 0.1:1 to 2:1.

5

Product Form

The final product form of hair treatment compositions according to the invention may suitably be, for example, 10 shampoos, conditioners, sprays, mousses, gels, waxes or lotions. Particularly preferred product forms are shampoos, post-wash conditioners (leave-in and rinse-off) and hair treatment products such as hair essences.

15 Shampoo compositions preferably comprise one or more cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair. Further surfactants may be present as emulsifiers.

20 Suitable cleansing surfactants, are selected from anionic, amphoteric and zwitterionic surfactants, and mixtures thereof. The cleansing surfactant may be the same surfactant as the emulsifier, or may be different.

- 6 -

Anionic Cleansing Surfactant

Shampoo compositions according to the invention will typically comprise one or more anionic cleansing surfactants 5 which are cosmetically acceptable and suitable for topical application to the hair.

Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, 10 alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The 15 alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule.

20

Typical anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl sulpho succinate, ammonium lauryl sulphosuccinate, ammonium lauryl

- 7 -

sulphate, sodium cocoyl isethionate, sodium lauryl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3), ammonium lauryl sulphate and ammonium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3).

The total amount of anionic cleansing surfactant in shampoo compositions of the invention is generally from 5 to 30, 10 preferably from 6 to 20, more preferably from 8 to 16 wt%.

Co-surfactant

The shampoo composition can optionally include co-surfactants, preferably an amphoteric or zwitterionic surfactant, which can be included in an amount ranging from 0 to about 8, preferably from 1 to 4 wt%.

Examples of amphoteric and zwitterionic surfactants include, 20 alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycimates, alkyl carboxyglycimates, alkyl amphopropionates, alkylamphoglycimates, alkyl amidopropyl hydroxysultaines,

- 8 -

acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl 5 sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

Another preferred co-surfactant is a nonionic surfactant, which can be included in an amount ranging from 0 to 8, 10 preferably from 2 to 5 wt%.

For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic (C₈ - C₁₈) primary or 15 secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

Further nonionic surfactants which can be included in shampoo 20 compositions of the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block

- 9 -

of one or more glycosyl groups. Preferred APGs are defined by the following formula:



5

wherein R is a branched or straight chain C₅ to C₂₀ alkyl or alkenyl group, G is a saccharide group and n is from 1 to 10.

Other sugar-derived nonionic surfactants which can be
10 included in shampoo compositions of the invention include the C₁₀-C₁₈ N-alkyl (C₁-C₆) polyhydroxy fatty acid amides, such as the C₁₂-C₁₈ N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide.

15

The shampoo composition can also optionally include one or more cationic co-surfactants included in an amount ranging from 0.01 to 10, more preferably from 0.05 to 5, most preferably from 0.05 to 2 wt%. Useful cationic surfactants
20 are described hereinbelow in relation to conditioner compositions.

- 10 -

The total amount of surfactant (including any co-surfactant, and/or any emulsifier) in shampoo compositions of the invention is generally from 5 to 50, preferably from 5 to 30, more preferably from 10 to 25 wt%.

5

Cationic Polymer

A cationic polymer may be present. The cationic polymer may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally 10 be between 5 000 and 10 000 000, typically at least 10 000 and preferably in the range 100 000 to about 2 000 000. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof.

Suitable cationic nitrogen polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition

The cationic conditioning polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

- 11 -

Suitable cationic conditioning polymers include, copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (CTFA name Polyquaternium-16); copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate, (CTFA name Polyquaternium-11); cationic diallyl quaternary ammonium-containing polymers in particular (CTFA Polyquaternium 6 and Polyquaternium 7, mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids as described in U.S. Patent 4,009,256; cationic polyacrylamides (as described in WO95/22311).

Cationic polysaccharide polymers suitable for use in compositions of the invention include those with an anhydroglucose residual group, such as a starch or cellulose. Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl

- 12 -

ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimonium chloride (commercially available from Rhone-Poulenc in their JAGUAR trademark series). Particularly preferred cationic polymers are JAGUAR C13S, JAGUAR C14, JAGUAR C15, JAGUAR C17 and JAGUAR C16 Jaguar CHT and JAGUAR C162.

The cationic conditioning polymer will generally be present in compositions of the invention at levels of from 0.01 to 5, preferably from 0.05 to 1, more preferably from 0.08 to 0.5 5 wt%.

- 13 -

Conditioning Surfactant

Conditioner compositions usually comprise one or more
5 conditioning surfactants which are cosmetically acceptable
and suitable for topical application to the hair.

Suitable conditioning surfactants are selected from cationic
surfactants, used singly or in admixture.

10

Cationic surfactants useful in compositions of the invention
contain amino or quaternary ammonium hydrophilic moieties
which are positively charged when dissolved in the aqueous
composition of the present invention.

15

Examples of suitable cationic surfactants are those
corresponding to the general formula:



20

in which R_1 , R_2 , R_3 , and R_4 are independently selected from (a)
an aliphatic group of from 1 to 22 carbon atoms, or (b) an
aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl,

- 14 -

aryl or alkylaryl group having up to 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate
5 radicals.

The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those
10 of about 12 carbons, or higher, can be saturated or unsaturated.

The most preferred cationic surfactants for conditioner compositions of the present invention are monoalkyl
15 quaternary ammonium compounds in which the alkyl chain length is C16 to C22.

Examples of suitable cationic surfactants include quaternary ammonium compounds, particularly trimethyl quaternary
20 compounds.

Preferred quaternary ammonium compounds include cetyltrimethylammonium chloride, behenyltrimethylammonium

- 15 -

chloride (BTAC), cetylpyridinium chloride,
tetramethylammonium chloride, tetraethylammonium chloride,
octyltrimethylammonium chloride, dodecyltrimethylammonium
chloride, hexadecyltrimethylammonium chloride,
5 octyldimethylbenzylammonium chloride,
decyldimethylbenzylammonium chloride,
stearyldimethylbenzylammonium chloride,
didodecyldimethylammonium chloride,
dioctadecyldimethylammonium chloride, tallowtrimethylammonium
10 chloride, cocotrimethylammonium chloride, PEG-2 oleylammonium
chloride and salts of these where the chloride is replaced
by halogen, (e.g. , bromide), acetate, citrate, lactate,
glycolate, phosphate nitrate, sulphate, or alkylsulphate.
Further suitable cationic surfactants include those materials
15 having the CTFA designations Quaternium-5, Quaternium-31 and
Quaternium-18. Mixtures of any of the foregoing materials
may also be suitable. A particularly useful cationic
surfactant for use in hair conditioners of the invention is
cetyltrimethylammonium chloride, available commercially, for
20 example as GENAMIN CTAC, ex Hoechst Celanese.

Salts of primary, secondary, and tertiary fatty amines are
also suitable cationic surfactants. The alkyl groups of such

- 16 -

amines preferably have from 12 to 22 carbon atoms, and can be substituted or unsubstituted.

Particularly useful are amido substituted tertiary fatty amines, in particular tertiary amines having one C₁₂ to C₂₂ alkyl or lakenyl chain. Such amines, useful herein, include

5 stearamidopropylidimethylamine,

stearamidopropylidiethylamine, stearamidoethylidethylamine,

stearamidoethylidimethylamine, palmitamidopropylid

10 imethylamine, palmitamidopropylidethylamine,

palmitamidoethylidethylamine, palmitamidoethylidimethylamine,

behenamidopropylidimethylamine,

behenamidopropylidethylamine, behenamidoethylidethylamine,

behenamidoethylidimethylamine,

15 arachidamidopropylidimethylamine, arachid

amidopropylidethylamine, arachidamidoethylidethylamine,

arachidamidoethylidimethylamine, diethylaminoethylstearamide.

Also useful are

dimethylstearamine, dimethylsoyamine, soyamine,

20 myristylamine, tridecylamine, ethylstearylamine, N-

tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and

arachidyl behenylamine.

- 17 -

These amines are typically used in combination with an acid to provide the cationic species. The preferred acid useful herein includes L- glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, 5 tartaric acid, citric acid, L-glutamic hydrochloride, and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055 to Nachtigal, et al., issued June 23, 1981.

10

The molar ratio of protonatable amines to H^+ from the acid is preferably from about 1:0.3 to 1:1.2, and more preferably from about 1:0.5 to about 1:1.1.

15

In the conditioners of the invention, the level of cationic surfactant is preferably from 0.01 to 10, more preferably 0.05 to 5, most preferably 0.1 to 2 wt% of the total composition.

20

The cationic surfactants detailed in this section are also suitable for use in the aspect of the invention wherein a cationic surfactant is intimately mixed with the

- 18 -

thermotropic mesogenic material and with oily conditioning material prior to the incorporation of the conditioning material into the final hair conditioning composition

5 **Fatty Materials**

Conditioner compositions of the invention preferably additionally comprise fatty materials. The combined use of fatty materials and cationic surfactants in conditioning 10 compositions is believed to be especially advantageous, because this leads to the formation of a structured phase, in which the cationic surfactant is dispersed.

By "fatty material" is meant a fatty alcohol, an alkoxyolated 15 fatty alcohol, a fatty acid or a mixture thereof.

Preferably, the alkyl chain of the fatty material is fully saturated.

20 Representative fatty materials comprise from 8 to 22 carbon atoms, more preferably 16 to 22. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and mixtures thereof. The use of these materials is also advantageous in

- 19 -

that they contribute to the overall conditioning properties of compositions of the invention.

Alkoxylated, (e.g. ethoxylated or propoxylated) fatty
5 alcohols having from about 12 to about 18 carbon atoms in
the alkyl chain can be used in place of, or in addition to,
the fatty alcohols themselves. Suitable examples include
ethylene glycol cetyl ether, polyoxyethylene (2) stearyl
ether, polyoxyethylene (4) cetyl ether, and mixtures
10 thereof.

The level of fatty alcohol material in conditioners of the
invention is suitably from 0.01 to 15, preferably from 0.1 to
10, and more preferably from 0.1 to 5 wt%. The weight ratio
15 of cationic surfactant to fatty alcohol is suitably from 10:1
to 1:10, preferably from 4:1 to 1:8, optimally from 1:1 to
1:7, for example 1:3.

Suspending Agents

20 In a preferred embodiment, the hair treatment composition,
especially if it is a shampoo composition, further comprises
from 0.1 to 5-wt% of a suspending agent. Suitable suspending
agents are selected from polyacrylic acids, cross-linked
polymers of acrylic acid, copolymers of acrylic acid with a
25 hydrophobic monomer, copolymers of carboxylic acid-containing
monomers and acrylic esters, cross-linked copolymers of

- 20 -

acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 5 carbon atoms and mixtures thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional 10 agent may also be used; they are available commercially as Carbopol 910, Carbopol 934, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trademark) materials are available from 15 Goodrich.

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that 20 available as Kelzan mu.

Conditioning Agents

Silicone Conditioning Agents

25 The compositions of the invention can contain emulsified droplets of a silicone conditioning agent, for enhancing conditioning performance.

- 21 -

Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes that have the CTFA designation dimethicone. Also suitable for use compositions of the invention (particularly shampoos and conditioners) 5 are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as are described for example in WO 96/31188.

10

The viscosity of the emulsified silicone itself (not the emulsion or the final hair conditioning composition) is typically at least 10,000 cst at 25 °C the viscosity of the silicone itself is preferably at least 60,000 cst, most 15 preferably at least 500,000 cst, ideally at least 1,000,000 cst. Preferably the viscosity does not exceed 10⁹ cst for ease of formulation.

20 Emulsified silicones for use in the shampoo compositions of the invention will typically have an average silicone droplet size in the composition of less than 30, preferably less than 20, more preferably less than 10 µm, ideally from 0.01 to 1 µm. Silicone emulsions having an average silicone

droplet size of $\leq 0.15 \mu\text{m}$ are generally termed microemulsions.

Examples of suitable pre-formed emulsions include emulsions 5 DC2-1766, DC2-1784, DC-1785 DC-1786 and microemulsions DC2-1865 and DC2-1870, all available from Dow Corning. These are all emulsions/microemulsions of dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation. A 10 preferred example is the material available from Dow Corning as DC X2-1787, which is an emulsion of cross-linked dimethiconol gum. A further preferred example is the material available from Dow Corning as DC X2-1391, which is a microemulsion of cross-linked dimethiconol gum.

15

A further preferred class of silicones for inclusion in shampoos and conditioners of the invention are amino functional silicones. By "amino functional silicone" is meant a silicone containing at least one primary, secondary 20 or tertiary amine group, or a quaternary ammonium group.

Examples of suitable amino functional silicones include: polysiloxanes having the CTFA designation "amodimethicone",

- 23 -

Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, DC2-8166, DC2-8466, and DC2-8950-114 (all ex Dow Corning), and GE 1149-75, (ex General Electric Silicones).

5 Suitable quaternary silicone polymers are described in EP-A-0 530 974. A preferred quaternary silicone polymer is K3474, ex Goldschmidt.

10 Also suitable are emulsions of amino functional silicone oils with non-ionic and/or cationic surfactant.

Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC929 Cationic Emulsion, DC939 Cationic Emulsion, and the 15 non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all ex Dow Corning).

With some shampoos it is particularly preferred to use a combination of amino and non amino functional silicones

20

The total amount of silicone is preferably from 0.01 to 10 %wt of the total composition more preferably from 0.3 to 5; most preferably 0.5 to 3-wt% is a suitable level.

(ii) **Non-silicone Oily Conditioning Components**

Compositions according to the present invention may also
5 comprise a dispersed, non-volatile, water-insoluble oily
conditioning agent.

By "insoluble" is meant that the material is not soluble in
water (distilled or equivalent) at a concentration of
10 0.1% (w/w), at 25°C.

Suitable oily or fatty materials are selected from
hydrocarbon oils, fatty esters and mixtures thereof.
Straight chain hydrocarbon oils will preferably contain from
15 about 12 to about 30 carbon atoms. Also suitable are
polymeric hydrocarbons of alkenyl monomers, such as C₂-C₆
alkenyl monomers.

Specific examples of suitable hydrocarbon oils include
20 paraffin oil, mineral oil, saturated and unsaturated
dodecane, saturated and unsaturated tridecane, saturated and
unsaturated tetradecane, saturated and unsaturated

- 25 -

pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used.

5

Suitable fatty esters are characterised by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols. Monocarboxylic acid esters include esters of alcohols and/or acids of the

10 formula R'COOR in which R' and R independently denote alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20. Di- and trialkyl and alkenyl esters of carboxylic acids can also be used.

15 Particularly preferred fatty esters are mono-, di- and triglycerides, more specifically the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as C₁-C₂₂ carboxylic acids. Preferred materials include cocoa butter, palm stearin, sunflower oil, soyabean oil and

20 coconut oil.

- 26 -

The oily or fatty material is suitably present at a level of from 0.05 to 10, preferably from 0.2 to 5, more preferably from about 0.5 to 3-wt%.

5 In hair treatment compositions containing a conditioning agent, it is preferred that a cationic polymer also be present.

Styling polymers

10 If the product is a styling product it is preferred if a styling polymer is present

15 The hair styling polymer if present is preferably present in the compositions of the invention in an amount of from 0.001% to 10% by weight, more preferably from 0.1% to 10% by weight, such as from 1% to 8% by weight.

20 Hair styling polymers are well known. Suitable hair styling polymers include commercially available polymers that contain moieties that render the polymers cationic, anionic, amphoteric or nonionic in nature. Suitable hair styling polymers include, for example, block and graft copolymers. The polymers may be synthetic or naturally derived.

- 27 -

Adjuvants

The compositions of the present invention may also contain adjuvants suitable for hair care. Generally such 5 ingredients are included individually at a level of up to 2, preferably up to 1 wt% of the total composition.

Suitable hair care adjuvants, include amino acids and ceramides.

10

The invention will now be further illustrated by the following, non-limiting Examples.

A number illustrates examples of the invention; a letter 15 illustrates Comparative Examples.

All percentages quoted are by weight based on total weight unless otherwise stated.

EXAMPLES

20

The following Examples were prepared:

- 28 -

Table 1

Shampoo

Ingredients	Wt %		
	Example A	Example 1	Example 2
Sodium lauryl ether sulphate (2EO)	12.0	12.0	12.0
Cocoyl amidopropyl dimethyl glycine	0	0	0
Silicone emulsion	2.0	2.0	2.0
Guar hydroxypropyl trimethylammonium chloride	0.30	0.30	0.30
Preservative	0.35	0.35	0.35
Perfume	0.42	0.42	0.42
Citric acid	0.17	0.17	0.17
Trimethyl glycine	1.20	-	-
Trehalose	-	1.0	0.4
Adipic acid	-	-	0.10
Succinic acid	-	0.50	-
Guanadine carbonate	-	-	0.10
Water and minors	to 100 wt%		

5

Results were obtained from a panel of sixty consumers. Each product was tested sequentially for a period of four days, with three days in-between, using a product without any actives. The results show consumer assessed scores of the

10 Examples relative to the Comparative Example.

- 29 -

The results are shown in figures 1 and 2. It is clearly shown that both Examples 1 and 2 have significant advantages over the comparative Example (Example A)

- 30 -

CLAIMS

1. A hair treatment composition comprising i) from 0.05 wt.% to 49 wt.% of a disaccharide; and ii) a di-acid.
5
2. A hair treatment composition according to claim 1 in which the disaccharide has two hexose rings.
3. A hair treatment composition according to any preceding 10 in which the disaccharide is selected from trehalose, cellobiose or mixtures thereof.
4. A hair treatment composition according to any preceding claim in which the disaccharide is trehalose.
15
5. A hair treatment composition according to any preceding claim in which the di-acid has the formula:

HOOC-(CH₂)_n-COOH

20 Where n is an integer from 2 to 8.
6. A hair treatment composition according to claim 5 where n equal to 2 or 4.
- 25 7. A hair treatment composition according to any preceding claim, which further comprises a guanidinium, salt.
8. A hair treatment composition according to claim 7 in which the guanidinium salt is a carbonate.
30

- 31 -

9. A hair treatment composition according to any proceeding claim further comprising a surfactant.
10. A hair treatment composition according to any preceding claim comprising an aqueous base.
- 5 11. Use of a composition according to any preceding claim for smoothing hair.
- 10 12. Use of a composition according to any one of claims 1 to 9 for aligning hair.
13. Use of a composition according to any one of claims 1 to 9 for preventing damage to the hair.
- 15 15. A method of treating hair by applying a composition according to any one of claims 1 to 9 to the hair.

1/1

Fig.1.

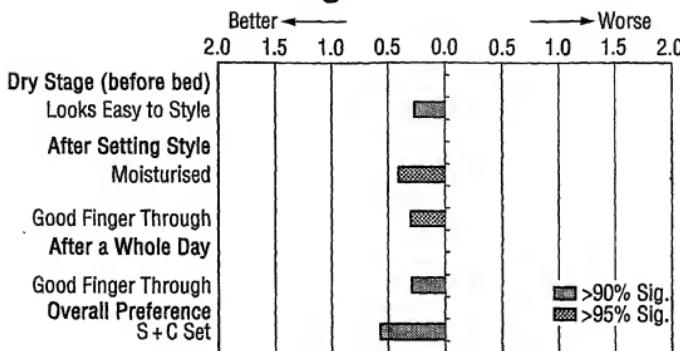
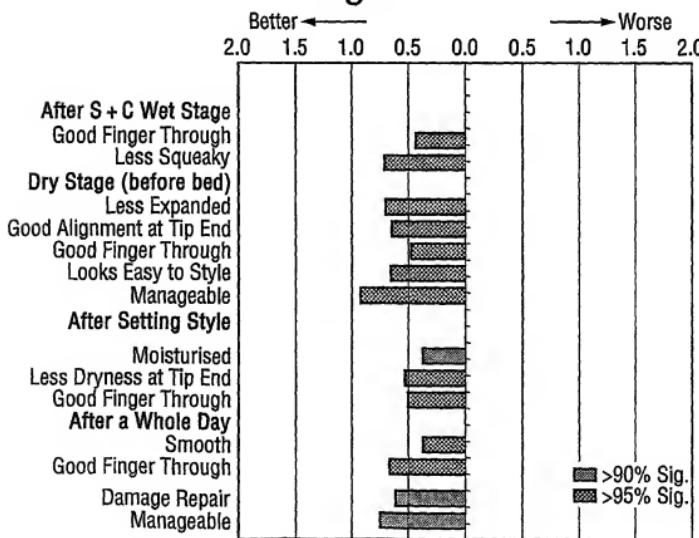


Fig.2.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/13701

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A61K7/06 A61K7/50		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 12 20 969 B (ERNST KRUEGERMEYER & CO SERUBA) 14 July 1966 (1966-07-14) claims 1,4; examples 1,2	1,2,9-15
X	WO 01/01948 A (ROBERT ALEXANDRE MICHEL ;ROBERT LADISLAS (FR); INST EVALUATION DER) 11 January 2001 (2001-01-11) example 4	1-6
X	EP 0 383 467 A (STRYDOM ANDRIES JOHANNES CORNE) 22 August 1990 (1990-08-22) page 4, line 8 - line 17	1,5,6, 11-15
A	US 6 348 200 B1 (UESAKA TOSHIO ET AL) 19 February 2002 (2002-02-19) claims 1,9,11; examples 12,13	1-15
		-/-
<input checked="" type="checkbox"/>	Further documents are listed in the continuation of box C.	<input type="checkbox"/> Patent family members are listed in annex.
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance		
E earlier document published on or after the International filing date		
L document which may throw doubts on priority (claim(s)) or which is cited to establish the publication date of another citation or other special reason (as specified)		
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the International filing date but later than the priority date claimed		
Date of the actual completion of the International search 20 April 2004		Date of mailing of the International search report 29/04/2004
Name and mailing address of the ISA European Patent Office, P.B. 6518 Patentlaan 2 NL - 2200 RD The Hague Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Voyatzoglou, D

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/13701

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00/40213 A (SAKO TAKASHI ; PROCTER & GAMBLE (US) 13 July 2000 (2000-07-13) claims 1,4,6 -----	1-15
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 03, 27 February 1998 (1998-02-27) & JP 09 291011 A (KOSE CORP), 11 November 1997 (1997-11-11) abstract -----	1-15
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 300 (C-449), 29 September 1987 (1987-09-29) & JP 62 091236 A (NIPPON OIL & FATS CO LTD; OTHERS: 01), 25 April 1987 (1987-04-25) abstract -----	1-6
A	DATABASE WPI Section Ch, Week 198649 Derwent Publications Ltd., London, GB; Class D21, AN 1986-322321 XP002241480 & JP 61 238894 A (SUNSTAR KK), 24 October 1986 (1986-10-24) abstract -----	1-6
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 01 29 January 1999 (1999-01-29) & JP 10 279449 A (NICHIDEN KAGAKU KK), 20 October 1998 (1998-10-20) abstract -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/13701

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
DE 1220969	B	14-07-1966	NL	6515171 A		26-05-1966
WO 0101948	A	11-01-2001	FR	2795956 A1		12-01-2001
			AU	6293200 A		22-01-2001
			WO	0101948 A2		11-01-2001
EP 0383467	A	22-08-1990	AU	4918790 A		09-08-1990
			CA	2009204 A1		06-08-1990
			EP	0383467 A2		22-08-1990
			JP	2282314 A		19-11-1990
			ZA	9000840 A		31-10-1990
US 6348200	B1	19-02-2002	JP	9110667 A		28-04-1997
			JP	9165313 A		24-06-1997
			JP	9208442 A		12-08-1997
			CN	1166135 A ,B		26-11-1997
			DE	69626629 D1		17-04-2003
			DE	69626629 T2		05-02-2004
			EP	0805674 A1		12-11-1997
			WO	9714401 A1		24-04-1997
			TW	453881 B		11-09-2001
WO 0040213	A	13-07-2000	WO	0040213 A1		13-07-2000
			AU	2309499 A		24-07-2000
JP 09291011	A	11-11-1997	NONE			
JP 62091236	A	25-04-1987	NONE			
JP 61238894	A	24-10-1986	NONE			
JP 10279449	A	20-10-1998	NONE			



Europäisches Patentamt
European Patent Office
Office européen des brevets

① Publication number:

0 304 846
A2

②

EUROPEAN PATENT APPLICATION

② Application number: 88113625.3

② Int. Cl. 1: A61K 7/06

② Date of filing: 22.08.88

② Priority: 28.08.87 US 90732

② Applicant: STERLING DRUG INC.

② Date of publication of application:
01.03.89 Bulletin 89/09

90 Park Avenue
New York New York(US)

② Designated Contracting States:
BE FR GB NL

② Inventor: Deshpande, Vikas Manohar

20 Birch Road
Ringwood New Jersey 07465(US)
Inventor: Waits, John Merrick
300 Parkway South
Clark New Jersey 07066(US)
Inventor: Decker, Susan Ahrendt
279 Botonin Avenue
Butler New Jersey 07405(US)

② Representative: Ballile, Iain Cameron et al
c/o Ladas & Parry Isartorplatz 5
D-8000 München 2(DE)

② Hair treatment composition.

② A composition for enhancing the body of hair comprising as essential ingredients in certain critical amounts an alkali metal or ammonium bisulfite, an alkanolamine, a guar hydroxypropyltrimonium chloride, a certain quaternary ammonium conditioner, an alkali metal or ammonium carbonate or an alkali metal phosphate and water; and a method of use thereof. The method comprises applying the composition to the hair, working it into the hair, lifting the hair with, e.g., the finger tips, a hair pick or the tail of a comb, allowing the composition to remain in contact with the hair for about 20 to 30 minutes, rinsing the hair and drying the hair.

EP 0 304 846 A2

The invention relates to a composition and method for improving the appearance and manageability of hair, more specifically to an aqueous foamable composition for conditioning and enhancing the body of hair.

5 Information Disclosure Statement

Men and women with so-called "limp" hair, that is, hair which is fine and relatively thin in diameter, have considerable difficulty in styling their hair under normal conditions of shampooing, drying and conditioning. Under higher relative humidity conditions, "limp" hair can become even "more limp" and therefore more difficult to style, manage and maintain in a particular styled configuration. Such difficulties can also be encountered in the case of normal and coarse hair. The need therefore exists for a convenient means for overcoming such difficulties, more specifically, for adding volume and fullness, i.e., body, to all types of hair.

It is known that systems for the permanent cold waving of hair can improve the body of hair, but such systems generally require that the hair be wound on curlers and/or rollers to impart curls and waves thereto, a time consuming operation. Such systems employ cold permanent waving compositions which contain reducing agents such as thiols, thioglyco lates, sulfites, bisulfites and sulfides. See for example the article on sulfite cold waving and hair straightening by W.R. Markland in Norda® Briefs, No. 492, July-August, 1979. Generally such cold permanent waving compositions are used in conjunction with rollers or rods in order to form curls or waves. Such compositions are employed in an amount, and left in contact with the hair for a time, sufficient to effect rupture of the disulfide linkage after which the composition is rinsed from the hair. The hair then generally is treated with a neutralizing (oxidizing) agent which results in the formation of new disulfide linkages. The cleaving of the disulfide linkages and subsequent formation of new disulfide linkages permits "permanent" shaping of the hair into desired configurations such as curls and waves. Cold permanent waving systems which employ rollers and/or curlers, a reducing agent and a neutralizing agent are described in U.S. Patents 3,864,476, 4,296,784 and 4,859,586.

U.S. Patents 3,966,903 and 4,504,468 describe cold permanent waving systems in which a neutralizing step is not required. The systems described in these patents also require the use of rods or curlers.

A 3-component cold permanent waving system currently in commercial use is OGILVIE Whisper 30 Wave™. The label contents of the three components are as follows:
 Waving Lotion 3 3/4 FL OZ.
 Contains: Water, Sodium Bisulfite, Monoethanolamine, Sodium Carbonate, TEA-coco-Hydrolyzed Protein a.
 Neutralizer 3 3/4 FL OZ.
 Contains: Water, PEG-150 Distearate b, Hydrogen Peroxide, Phosphoric Acid; Tetrasodium Pyrophosphate, 35 Sodium Stannate.

a) the triethanolamine salt of the condensation product of coconut acid chloride and
 40 Hydroized Animal Protein (CTFA Cosmetic Ingredient Dictionary, Third Edition, page 312)

b) $\text{CH}_3(\text{CH}_2)_{15}\text{CO}-(\text{OCH}_2\text{CH}_2)_n\text{O-CO}(\text{CH}_2)_{15}\text{CH}_3$, n = average of 150 (CTFA Cosmetic Ingredient Dictionary, Third Edition, page 209)

45 c) $\text{RCO-NH-(CH}_2)_2-\text{N}(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{OH Cl}^-$ (CTFA Cosmetic Ingredient Dictionary, Third Edition, page 268)

d) 3-(D-glucuronamino)-N-(2-hydroxyethyl)-N,N-dimethyl-1-propanaminium
 50 chloride (CTFA Cosmetic Ingredient Dictionary, Third Edition, pages 267-268)

e) $\text{CH}_3(\text{CH}_2)_{15}\text{CO-NH-CH}_2\text{-C(H)}(\text{CH}_2)\text{-OCH}_2\text{CH}_2\text{OH}$ (CTFA Cosmetic Ingredient Dictionary, Third Edition, page 128)

55 f) a mixture of dimethicone with an average chain length of 200 to 350 dimethylsiloxane units and silica gel (CTFA Cosmetic Ingredient Dictionary, Third Edition, page 278). Dimethicone is a mixture of fully methylated linear siloxane polymers end blocked with trimethylsiloxy units (CTFA Cosmetic Ingredient Dictionary, Third Edition, page 83)

PERM-SOFTTM 1/2 FL. OZ.

Contains: Water, Quaternium-26 c, Propylene Glycol, Quaternium-22 d, Lactic Acid, Sodium Laureth Sulfate, Hydroxyethyl Stearamide-MIPA, e Fragrance, Simethicone f, Methylparaben, Sorbic Acid, D&C Yellow No. 10.

5 In cold permanent waving hair with Ogilvie Whisper Wave™, the hair is wound on rods, the waving lotion is then applied to the hair and allowed to remain on the hair for between 30 and 60 minutes, the hair is then rinsed well and, with the rods still in place, is treated with the neutralizer. The rods then are removed and the hair is rinsed, blotted dry, conditioned with the PermSoft™ and styled.

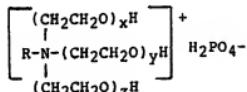
An almost inevitable result of exposing hair to waving or straightening compositions is a deterioration in 10 tactile properties, "feel", manageability and combability of the hair due to tangling. It is therefore common practice to treat the hair with one or more conditioning agents to ameliorate the situation. Such conditioning agents are generally incorporated in the neutralizer or added after the neutralizing step, although the incorporation of certain conditioners in the reducing composition or in a composition for application to the hair prior to the reducing step have been described. See U.S. Patents 3,912,808, 4,390,033, 4,391,286, 15 4,416,287, 4,428,375 and 4,602,848 and UK Patent Application GB 2068310 A.

U.S. Patent 4,243,659 describes compositions for Improving hair body comprising an aqueous solution 20 of a hair cleansing synthetic detergent containing a bisulfite salt and dimethylurea as a hair swelling agent. The compositions preferably contain a cationic hair conditioner. The method of using the composition involves applying it to the hair after a preliminary shampoo and rinse with the composition, allowing it to remain on the hair for from 3 to 20 minutes, rinsing it from the hair, and drying the hair and then styling it.

SUMMARY OF THE INVENTION

26 This Invention resides in the discovery of a composition comprising a bisulfite salt, an alkanolamine, an alkalinizing agent, a combination of specific cationic conditioning agents and water which when used to treat hair in accordance with a specific process, provides added volume and fullness, i.e., body, to all types of hair without the need to resort to rollers or curlers, while at the same time conditioning the hair. This added 30 volume and fullness lasts for a period of four to six weeks.

In one aspect of the Invention there is provided a composition for enhancing the body of hair comprising (a) from about 5 to about 10 percent by weight of an alkali metal bisulfite or ammonium bisulfite; (b) from about 2 to about 5 percent by weight of a mono-, di- or tri-alkanolamine; (c) from about 0.1 to 35 about 1.5 percent by weight of guar hydroxypropyltrimonium chloride having a viscosity of 75 to 150 cps or a guar hydroxypropyltrimonium chloride having a viscosity of 2500 to 3200 cps; (d) from about 0.2 to about 1 percent by weight of a quaternary ammonium compound selected from the group consisting of a compound conforming to the formula:



40 wherein $x+y+z$ has an average value of 10 and R is a straight-chain alkyl radical having from 6 to 18 carbon atoms or mixtures of such radicals, laurdimonium hydrolyzed animal collagen, cocodimonium hydrolyzed animal collagen and stearidimonium hydrolyzed animal collagen; and (e) water sufficient to make 100%; provided that when (a) is alkali metal bisulfite, the ion additionally comprises (f) from about 0.75 to about 3 percent by weight of an alkali metal carbonate, ammonium carbonate or an alkali metal phosphate.

In a second aspect of the invention there is provided a method for enhancing the body of hair which comprises, in sequence, the following steps: (1) applying to the hair the composition described above; (2) working the composition into the hair until the composition is distributed throughout the hair; (3) lifting the hair, (4) allowing the composition to remain in contact with the lifted hair for from about 20 to about 30 minutes; (5) rinsing the hair with water sufficient to remove the composition from the hair; and (6) drying the hair.

The composition of the invention, when applied to hair, swells individual hair fibers, increases the frictional coefficient and surface roughness of the hair thereby increasing hair volume and also provides

conditioning to the hair, and when used in accordance with the method of the invention, enhances the body (fullness) of the hair to an unexpected degree. Thus the composition and method of the invention provide a convenient one-step procedure, i.e., as opposed to procedures involving two or more steps wherein subsequent treatment of the hair with further compositions such as neutralizers and conditioners is required, 5 for enhancing the body of the hair while at same eliminating the need for using such devices as rollers and rods.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING THE PREFERRED EMBODIMENTS

10

The composition of the invention comprises as essential ingredients in critical amounts a water-soluble bisulfite salt, an alkanolamine, two quaternary ammonium compounds, water and, when the bisulfite salt is an alkali metal bisulfite, a carbonate or phosphate buffering agent.

15

Bisulfite Salt

20 The bisulfite salt is selected from alkali metal bisulfites, such as sodium and potassium bisulfite, and ammonium bisulfite and mixtures thereof. The bisulfite functions as a reducing agent which chemically ruptures the disulfide linkages of cystine present in hair. The bisulfite salts are active at low to moderate temperatures (20°-45° C.), essentially odorless and can be formulated into the composition of the invention over a wide range of pH. The bisulfite salt is employed at a concentration of from about 5 to about 10 25 percent by weight of the composition.

Alkanolamine

30

The alkanolamine is selected from mono-, di- and tri-alkanolamines, wherein alkanol is straight or branched and has from 1 to 3 carbon atoms, for example monoethanolamine, diethanolamine, triethanolamine, isopropanolamine and diisopropanolamine and mixtures thereof. The alkanolamine is an alkalinizing agent which functions to adjust the pH of the composition of the invention. The 35 pH of the composition should be in the range of about 6.8 to about 10. The alkanolamine also accelerates the chemical rupture of the disulfide linkages by penetrating and swelling the hair fibers thus facilitating entrance of the bisulfite reducing agent into the hair cuticle. The alkanolamine is employed at a concentration of from about 2 to about 5 percent by weight of the composition.

40

Quaternary Ammonium Compounds

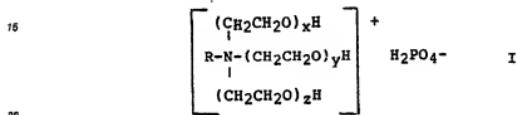
The composition of the invention comprises two quaternary ammonium compounds, both of which 45 function as hair conditioners and one of which additionally functions as a thickening agent.

The quaternary ammonium compound which functions as a hair conditioning agent as well as a thickening agent is a cationic guar gum having the CTFA adopted name "guar hydroxypropyltrimonium chloride". In the CTFA Cosmetic Ingredient Dictionary, Third Edition (hereafter "CTFA Dictionary"), page 117, guar hydroxypropyltrimonium chloride is defined as a quaternary ammonium derivative of 50 "hydroxypropyl guar" which in turn, at page 128, is defined as a propylene glycol ether of "guar gum". Guar gum, is a galactomannan with a structure composed of a straight backbone chain of D-mannopyranose units with a side branching unit of D-galactopyranose on every other unit. The average molecular weight of guar gum is in the range of 200,000 to 300,000. Two specific guar hydroxypropyltrimonium chlorides are employed in the composition of the invention. One has a viscosity of from 75 to 55 150 cps (1% aqueous solution @ 25° C., using a Brookfield RVF @ 20 RPM) and a pH of 9 to 11 (1% aqueous solution) and the other viscosity of from 2500 to 3200 cps (1% aqueous solution @ 25° C., using a Brookfield RVF @ 20 RPM) and a pH of 7.5 to 11 (1% aqueous solution). The guar hydroxypropyltrimonium chloride having the lower viscosity is preferred at lower pH values of the composition and the one having

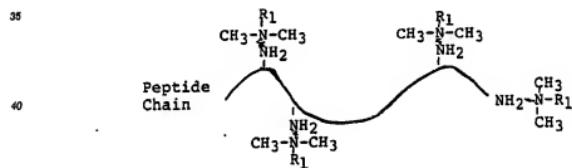
the higher viscosity is preferred at the higher pH values. These guar hydroxypropyltrimonium chlorides are sold under the designations respectively Jaguar C-15 and Jaguar C-17, by Celanese Plastics and Specialties Company. Mixtures of these guar hydroxypropyltrimonium chlorides may be used. The guar hydroxypropyltrimonium chloride is employed at concentrations of from about 0.1 to about 1.5 percent by weight based on the total weight of the composition.

15 The upper limit of concentration in the composition of the guar hydroxypropyltrimonium chloride is governed by the degree of thickening to be imparted to the composition. As a result, the range of concentrations at which it may be employed, as defined above, is not fully adequate to provide the desired degree of hair conditioning. It is therefore essential to augment conditioning with a second conditioner which 10 is compatible with the guar hydroxypropyltrimonium chloride.

The second conditioner is selected from a quaternary ammonium compound selected from a compound conforming to the formula:



wherein $x+y+z$ has an average value of 10 and R is a straight-chain alkyl radical have from 6 to 18 carbon atoms or mixtures of said alkyl radicals, laurdimonium hydrolyzed animal collagen, cocodimonium hydrolyzed animal collagen and steardimonium hydrolyzed animal collagen and mixtures thereof. The CTFA 25 Adopted Name for the compound of Formula I is Quaternium-52 which is defined in the CTFA Dictionary as for Formula I above. Quaternium-52 is sold under the designation DEHYQUART SP by Henkel Corporation. Laurdimonium hydrolyzed animal collagen, cocodimonium hydrolyzed animal collagen (CTFA Adopted Name) and steardimonium hydrolyzed animal collagen (CTFA Adopted Name) are multi-functional highly 30 cationic alkyl quaternary short chain protein derivatives which combine in one molecule a low molecular weight collagen hydrolysate, fatty radicals and quaternary groups. The low molecular weight parent hydrolysate is prepared such that the basic amino groups in collagen (arginine, histidine, lysine, etc.) are available for quaternization. A pictorial representation of these compounds is as follows:



45 where for laurdimonium R_1 is a C_{12-18} fatty radical, for cocodimonium R_1 is a C_{12-18} fatty radical and for 50 steardimonium R_1 is a C_{18} fatty radical. Laurdimonium hydrolyzed animal collagen, cocodimonium hydrolyzed animal collagen and steardimonium hydrolyzed animal collagen each have an isoinic point of approximately 11 and a pH (10% aqueous solution) of from 4.0 to 5.5. They are sold under the designations respectively Croquat L, Croquat M and Croquat S by Croda Inc. The second quaternary conditioner is employed in the composition at a concentration of from about 0.2 to about 1 percent by weight based on the total weight of the composition.

Buffering Agent

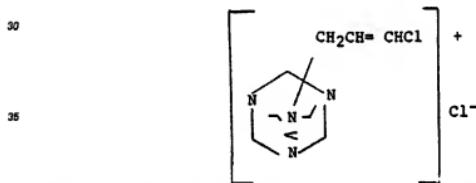
In order to maintain the pH of the composition in the above-specified range, it is necessary to include in those compositions of the invention which employ an alkali metal bisulfite as reducing agent, a buffering agent. The buffering agent is selected from alkali metal carbonate such as sodium or potassium carbonate, alkali metal phosphate, such as mono-, di- or tri-sodium or potassium phosphate or mixtures thereof. When ammonium bisulfite is employed as reducing agent in the composition it has been found that a buffering agent may be dispensed with since such compositions are self-buffering. However, carbonate and phosphate buffering agents may be employed if desired. The buffering agent is employed in the composition in a concentration of from about 0.75 to about 3 percent by weight based on the weight of the composition.

The final essential ingredient of the composition is water, preferably deionized water. The water is added to the other essential ingredients and any optional ingredients, described hereinafter, in a concentration sufficient to make 100%.

Optical Ingredients

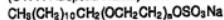
The composition of the invention may include effective amounts of optional ingredients in order to impart additional desirable properties and/or aesthetic appeal to the composition such as additional hair conditioners, preservatives, fragrances, opacifiers, wetting agents, emollients, etc.

As preservatives there may be employed, for example, methylparaben, ethylparaben, or propylparaben, disodium ethylene-diaminetetraacetic acid (disodium EDTA) and Quaternium-15 (CTFA Adopted Name) and mixtures thereof. Quaternium-15 is defined in the CTFA Dictionary as a quaternary ammonium salt which conforms to the formula:



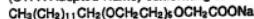
where n has an average value of 150. PEG-150 also adds body, i.e., a nice smooth feel, to the composition. The emollients may be employed at a concentration of from about 0.5 to about 5 percent by weight of the composition.

As opacifier there may be employed anionic surfactants or a combination of an anionic surfactant with 5 a nonionic surfactant. As anionic surfactant there may be employed for example, sodium lauryl sulfate (CTFA Adopted Name) which conforms to the formula (CTFA Dictionary):



where n averages between 1 and 4. This chemical is sold under the designation Standapol ES by Henkel, Inc.

10 A further anionic surfactant that may be employed as an opacifier is sodium trideceth-7 carboxylate (CTFA Adopted Name) conforming to the formula (CTFA Dictionary):



This chemical is sold under the designation Sandopan DTC by Sandoz, Inc. Colors and Chemicals Division.

15 The opacifiers may be employed in the composition in a concentration of from about 0.5 to about 1.5 percent by weight of the composition.

The compositions may be formulated as lotions, mousse, gels, creams or aerosols. When the essential ingredients are mixed in the concentrations specified hereinbefore, they are obtained either as dispersions in the form of lotions or gels. A gel can be obtained if the guar hydroxypropyltrimonium chloride is used in 20 a concentration falling at the upper end of the specified concentration range, i.e., from about 1.4 to 1.5 weight per cent, while a lotion (liquid) can be obtained at lower concentrations of the guar hydroxypropyltrimonium chloride. The composition can be obtained in the form of a cream by adding thereto an effective amount of an opacifier as described hereinbefore, i.e., at a concentration of from about 0.5 to about 1.5 percent by weight. The composition in the form of a liquid can be formulated as an aerosol which, on 25 dispensing from a conventional aerosol dispenser, is obtained in the form of a creamy foam known in the art as a mousse. Such compositions include conventional aerosol propellants, such as a hydrocarbon, for example isobutane, or a halocarbon, for example 1,1-difluoroethane, and mixtures thereof, in amounts effective to permit substantially complete evaporation of the composition from the aerosol container. The amount of any particular aerosol propellant or mixture of propellants to be employed can readily be determined by one of ordinary skill in the art.

30 The composition of the invention preferably is applied to damp hair, e.g., after a shampoo and towel drying. The composition then is worked into and evenly distributed throughout the hair by massage (shampooing) until a thick foam results. The foam is essential for achieving maximum enhanced body and volume of the hair. Thus when in the method of the invention the hair is lifted away from the scalp, the foam 35 functions to maintain the hair in the lifted position throughout the entire time the composition remains in contact with the hair. This results in an unexpected increase in the body and volume of hair over and above that which results solely from the swelling of the hair fiber if left lie flat against the scalp and precludes the need for rollers and rods. However, if the composition is in gel form, foaming, although preferred, is not essential since the gel as such can maintain the hair in the lifted position. If desired, a plastic cap may be 40 used to cover the hair after it has been treated with the composition and lifted in order to hasten the body enhancing process. Since the ruptured disulfide linkages in the hair can be allowed to reform by air oxidation rather than the use of a neutralizer such as hydrogen peroxide, the method of the invention provides a convenient one-step procedure for enhancing the body of hair. The air oxidation preferably is accelerated by blow drying the hair at elevated temperatures using conventional blow drying techniques. Of 45 course, if desired, the hair may, after completion of the method of the invention, be treated with a suitable oxidizing agent such as hydrogen peroxide in order to eliminate slight odors which may be imparted to the hair during the cleaving of the disulfide linkages by the reducing agent. However, such odors as may be present on the hair generally will dissipate naturally at ambient temperatures in about 24 hours after treatment.

50 Lifting of the hair in the method of the invention can be accomplished by such means as the finger tips, a plastic hair pick or the tail of a comb, the lifting being performed on portions of the hair comprising strands of hair in various numbers. Using such means, the hair may, according to individual tastes, be lifted in straight form, or shaped gently, for example, into bends, waves or curls. If desired, plastic clips may be employed. In the case of long hair, the hair can be loosely piled on top of the head and secured with plastic 55 clips. It will be understood that the term lifting the hair as used herein means lifting the hair in either straight or shaped (e.g., bent, waved or curled) configuration without the use of rods or curlers.

On completion of the method of the invention the hair may be shampooed with a conventional shampoo (which may contain a small amount of hydrogen peroxide) to give the perception of cleaner hair and to help

remove any residual odor. The hair then may be styled in any desired fashion without any perceived loss of enhanced body.

The enhanced body imparted to the hair by the method of the invention is perceived by the consumer to remain with the hair for a period of from about 4 to 8 weeks, even with repeated shampoos and 5 stylings.

The compositions, when used in accordance with the method of the invention, are retained on the hair, after having been distributed evenly throughout the hair as a foam, for from about 20 to about 30 minutes, the latter time in the case of "normal" hair and for shorter periods, down to about 20 minutes, for hair which has been recently colored, the timing being dependent on how recently the coloring was performed.

10 The compositions of the invention are adapted for use on human hair in the home as well as in beauty salons.

The compositions may be formulated at ambient temperatures by combining the ingredients thereof in any order using conventional mixing techniques such as stirring. A convenient process is as follows (stirring maintained throughout the process):

15 The hydroxypropyltrimonium chloride is added to the water and after 15 to 20 minutes the bisulfite salt is added. After about 5 minutes there are added in sequence the alkanolamine, the carbonate (or phosphate), the carbonate being added at a rate to avoid excess foaming, and finally the quaternary ammonium compound (conditioning agent). Any optional ingredients may be added at the end of the process or at intermediate stages thereof. Stirring is then continued for about 15 minutes after which the 20 process is completed.

The compositions may be packaged in and dispensed from conventional packages and dispensers such as aerosol dispensers (in combination with a aerosol propellant system) or, such as in the case of gels, squeeze tubes, or, such as in the case of liquids, squeeze bottles, such dispensers having or being fitted with suitable dispensing openings as are conventional in the art.

25 The following examples are illustrative of the compositions of the invention without, however, being limited thereto.

Specific compositions with varying concentrations of ingredients falling within the ranges of weight-percent concentrations specified for Examples I, II and III in the table below were formulated:

30		Weight-Percent ^a		
Example:		I	II	III
Ingredient				
	Sodium bisulfite	5.0-10.0	5.0-10.1	-
	Ammonium bisulfite			6.75-9.0
35	Monoethanolamine	---	q.s. to pH 6.8-10 ^b ---	---
	Guar hydroxypropyltrimonium chloride	---	0.1-1.5	---
	Quaternary compound of Formula I	0.1-0.50	-	0.1-0.50
40	Laurdimonium (or cocodimonium or steardimonium) hydrolyzed animal collagen		0.08-0.60	-
	Sodium carbonate	0.75-2.0	0.75-2.0	-
	Ammonium carbonate	-	-	1.0-3.0
	Urea	---	5.0-15.0	---
45	TEA-coco-hydrolyzed animal protein	0.08-0.80	-	0.08-0.80
	Sodium laureth sulfate or sodium trideceth-7 carboxylate	-	0.5-1.5	0.5-1.5 ^c
50	PEG-150 distearate or lactamide MEA	-	1.0-5.0	-
	Deionized water	---	q.s. to 100% ^d	---

a) Based on 100% active ingredient

b) Approximately 2.0-5.0 wt-%

c) Sodium laureth sulfate

d) Approximately 65-85 wt-%

The following specific examples were prepared:

Example IV

Ingredient	Weight-%
Sodium bisulfite	7.70
Monethanolamine	3.94
Guar hydroxypropyltrimonium chloride ^a	0.20
Quaternary compound of Formula I ^b	0.50
Sodium carbonate	1.50
TEA-coco-hydrolyzed animal protein ^c	0.90
Deionized water	85.36
pH 8.2	100.00

a) Jaquar C-17
 b) Dehyquart SP
 c) Lexein® S-820TA

The composition of Example IV was formulated as an aerosol having the following composition:

Composition of Example IV 90.5 wt-%

Propellant 9.5 wt-%

The propellant consisted of 60 parts by weight of isobutane and 40 parts by weight of 1,1-difluoroethane (HYDRO-FLUOROCARBON 152A).

The aerosol composition when dispensed from a conventional aerosol container fitted with an appropriate dispensing button is in the form of a mousse.

When used on human subjects having fine, normal and coarse hair in accordance with the method of the invention, the aerosol composition substantially enhanced the body (fullness and volume) as well as the manageability of the hair in most cases.

Examples V and VI are as follows:

Ingredient	Weight-%	
	V	VI
Sodium bisulfite	8.60	-
Ammonium bisulfite	-	9.00
Monethanolamine	2.80	2.20
Guar hydroxypropyltrimonium chloride ^a	0.20	0.20
Quaternary Compound of Formula I ^b	0.25	0.25
Sodium carbonate	1.40	-
Urea	5.00	5.00
TEA-coco hydrolyzed animal protein ^c	0.80	0.80
Fragrance	0.50	0.50
Quaternium-15 ^d	0.10	0.10
Methylparaben	0.10	0.10
Disodium EDTA	0.02	0.02
Deionized water	q.s. to 100%	
pH	approx. 7.4	approx. 6.8

a),b) and c) - see Example IV

d) Dowicil 200

In each of Examples IV, V and VI the weight-percent is based on 100% active ingredient.

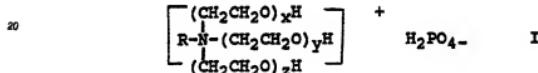
The compositions of Examples I to VI were formulated according to the process described hereinbefore. In Example I the urea was added immediately after the monethanolamine and the TEA-coco-hydrolyzed animal protein was added immediately after the carbonate. In Example II the urea was added after the guar hydroxypropyltrimonium chloride and the lactamide MEA or PEG-150 distearate and the sodium laureth

sulfate or sodium trideceth-7 carboxylate were added in sequence immediately after the quaternary ammonium compound. In Example III the TEA-coco-hydrolyzed animal protein, the sodium trideceth-7 carboxylate and the urea were added in sequence after the guar hydroxypropyltrimonium chloride. In Example IV the TEA-coco-hydrolyzed animal protein was added after the bisulfite. In Examples V and VI the urea was added after the guar hydroxypropyltrimonium chloride, the TEA-coco-hydrolyzed animal protein after the bisulfite and the fragrance and preservatives, in the sequence indicated, at the end.

Claims

10

1. A composition for enhancing the body of hair comprising:
 - (a) from about 5 to about 10 percent by weight of an alkali metal bisulfite or ammonium bisulfite;
 - (b) from about 2 to about 5 percent by weight of monoalkanolamine, dialkanolamine or trialkanolamine wherein the alkanol radical in each instant has from 1 to 3 carbon atoms;
 - (c) from about 0.1 to about 1.5 percent by weight of guar hydroxypropyltrimonium chloride;
 - (d) from about 0.2 to about 1 percent by weight of a quaternary ammonium compound which is a compound conforming to the formula:



25. wherein $x+y+z$ has an average value of 10 and R is a straight-chain alky radical having from 18 to 18 carbon atoms and mixtures of said radicals; laurdimonium hydrolyzed animal collagen, cocodimonium hydrolyzed animal collagen or steardimonium hydrolyzed animal collagen; and
 - (e) water sufficient to make 100%; provided that when (a) is an alkali metal bisulfite, the composition additionally comprises
 - (f) from about 0.75 to about 3 percent by weight of an alkali metal carbonate, ammonium carbonate or an alkali metal phosphate.
30. 2. The composition of claim 1, wherein the alkanolamine is monoethanolamine.
3. The composition of claim 1 or 2, wherein the alkali metal carbonate is sodium carbonate.
4. The composition according to any one of the preceding claims, which additionally includes urea, usually in a concentration of from about 5 to about 15 percent by weight.
35. 5. A composition according to any one of the preceding claims, which additionally includes an opacifying agent, usually in a concentration of from about 0.5 to about 1.5 percent by weight.
6. A composition according to claim 1, consisting essentially of from 5.0 to 10.0 weight-percent of sodium bisulfite, from 2.0 to 5.0 weight-percent of monoethanolamine, from 0.1 to 1.50 weight-percent of 40 guar hydroxypropyltrimonium chloride, from about 0.75 to 2.0 weight-percent of sodium carbonate, from 5.0 to 15.0 weight-percent of urea, from 0.08 to 0.80 weight-percent of TEA-coco-hydrolyzed animal protein and the remainder to 100% water.
7. A composition according to claim 1, consisting essentially of from 5.0 to 10.1 weight-percent of 45 sodium bisulfite, from 2.0 to 5.0 weight-percent of monoethanolamine, from 0.1 to 1.5 weight-percent of guar hydroxypropyltrimonium chloride, from 0.08 to 0.60 weight-percent of laurdimonium hydrolyzed animal collagen, cocodimonium hydrolyzed animal collagen or steardimonium hydrolyzed animal collagen, from 0.75 to 2.0 weight-percent of sodium carbonate, from 5.0 to 15.0 weight-percent of urea, from 0.5 to 1.5 weight-percent of sodium laureth sulfate or sodium trideceth-7 carboxylate, from 1.0 to 5.0 weight-percent of PEG-150 distearate or lactamide MEA and the remainder to 100% water.
8. A composition according to claim 1, consisting essentially of from 6.75 to 9.0 weight-percent of 50 ammonium bisulfite, from 2.0 to 5.0 weight-percent of monoethanolamine, from 0.1 to 1.5 weight-percent of guar hydroxypropyltrimonium chloride, from 0.1 to 0.50 weight-percent of the quaternary ammonium compound of Formula I, from 0.1 to 3.0 weight-percent ammonium carbonate, from 5.0 to 15.0 weight-percent of urea, from 0.08 to 0.8 weight-percent of TEA-coco-hydrolyzed animal protein, from 0.5 to 1.5 weight-percent of sodium laureth sulfate and the remainder to 100% water.

9. A composition according to any one of the preceding claims, which includes an effective amount of a preservative, e.g., about 0.1 weight-percent of Quaternium-15, about 0.10 weight-percent of methylparaben and about 0.02 weight-percent disodium EDTA.

10. A method for enhancing the body of hair comprising in sequence the following steps:

- 5 (1) applying to the hair a composition according to any one of the preceding claims;
- (2) working the composition into the hair until the composition is distributed throughout the hair;
- (3) lifting the hair;
- (4) allowing the composition to remain in contact with the hair for from about 20 to about 30 minutes;
- (5) rinsing the hair with water sufficient to remove the composition from the hair; and
- 10 (6) drying the hair.

15

20

25

30

35

40

45

50

55

